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LXIX.—*The Action of Alcohol on the Sulphates of Sodium.*

By GERALD SNOWDEN BUTLER and HORACE BARRATT DUNNICLIFF.

THE literature dealing with the solubility relationships of the sulphates of sodium is given by Foote (*J. Ind. Eng. Chem.*, 1918, 10, 896), and Saxton (*ibid.*, 897) draws certain important conclusions relating to the composition of the solid sulphates of sodium prepared according to a method by which these were washed first with a mixture of sulphuric acid, water, and alcohol, then with alcohol, and finally with ether.

The present paper shows (1) that sodium sulphate and sodium hydrogen sulphate are acted on by a mixture of alcohol and sulphuric acid, and (2) that the washing with alcohol would decompose sodium hydrogen sulphate alone or in the presence of sodium sulphate, but would not decompose the compound $\text{Na}_2\text{SO}_4\cdot\text{NaHSO}_4$. Saxton does not state how many times his compounds were washed with alcohol or ether, or if the washing was continued until the washings were neutral. It is shown below that, with or without preliminary washings with alcohol, many days' extraction with ether are required completely to remove the acidity from sodium sulphate or hydrogen sulphate which has been treated with alcoholic sulphuric acid. This point appears to be of great importance in connexion with the results given in Saxton's paper.

Lunge ("Sulphuric Acid and Alkali," 1909, Vol. II, Part I, 29) states that the compound $\text{Na}_3\text{H}(\text{SO}_4)_2$, observed by Thomson and Mitscherlich, is stable in air (see also D'Ans, *Ber.*, 1906, 39, 1534), that (*loc. cit.*, p. 24) water decomposes sodium hydrogen sulphate into neutral sulphate and free sulphuric acid (compare Pascal and Ero, *Bull. Soc. chim.*, 1919, [iv], 25, 25), and that alcohol deprives powdered sodium hydrogen sulphate of all free acid (see also Roscoe and Schorlemmer's "Treatise on Chemistry," 1913, Vol. II, pp. 261 and 341, where a similar statement is made regarding potassium hydrogen sulphate).

Pascal and Ero (*loc. cit.*) have studied the ternary system $\text{Na}_2\text{SO}_4\text{--H}_2\text{SO}_4\text{--H}_2\text{O}$. They state that a fused mixture of sodium sulphate and hydrogen sulphate is converted on cooling through 179° into the compound $\text{Na}_2\text{SO}_4\cdot\text{NaHSO}_4$. Further, that nitre-cakes having an acidity inferior to 36 per cent. of sulphuric acid, on cooling after the retort is tapped, must pass through that temperature, and must therefore consist of a mixture of sodium hydrogen sulphate and the compound $\text{Na}_2\text{SO}_4\cdot\text{NaHSO}_4$.

EXPERIMENTAL.

This work was undertaken as part of a research on the recovery of sulphuric acid from nitre-cake by means of spirits of wine (commercial ethyl alcohol). Experiments on commercial nitre-cakes were somewhat anomalous, but showed that nitre-cake, whether dry or moistened with 10 per cent. of water, when washed with either commercial (undried) alcohol or with absolute alcohol gave a residue having an acidity corresponding with about 18.7 per cent. of sulphuric acid, and that even in cases where the water added to the nitre-cake was as much as 60 per cent. of the weight of the cake, the residue had an acidity of about that value.

In view of the statements mentioned above regarding the action of alcohol on sodium hydrogen sulphate, it was expected that the residues resulting from these experiments would be free from acid. The fact that they invariably showed an acidity approximating to 18.5 per cent. suggested the formation of an acid salt having an acidity inferior to that of sodium hydrogen sulphate. The subsequent work was undertaken with the object of elucidating this point.

It is now known, as the result of this work, that exhaustive extraction of nitre-cake by commercial alcohol containing even small percentages of water leads to the progressive diminution in the acidity of the residue after each extraction, and finally results in complete extraction of the acid. The constancy of the value (about 18.5 per cent.) obtained in the above experiments is due to the fact that the residues were not washed exhaustively with alcohol. Washing with the alcohol was only repeated four or five times. The progressive extraction of nitre-cake by commercial spirit has been studied by the authors, and the acidity in the residue after each extraction has been determined. Full details of this part of the work will be published in a subsequent paper on the commercial aspect of the subject, but the values given in table I will illustrate the points sufficiently for the present purpose, and will explain one of the several reasons why an investigation of the subject with pure materials was undertaken.

TABLE I.

Successive Extraction of Nitre-cake by Moist Alcohol. (About 5 per cent. of Water.)

					Sulphuric acid. Per cent.
Acidity of original cake					33.0
Acidity of residue after 6th extraction with alcohol...					16.4
" " 12th " "				...	8.8
" " 18th " "				...	1.6

It will be shown that pure, dry alcohol extracts acid from pure sodium hydrogen sulphate until the residue contains only 18.69 per cent. (calc.: 18.7 per cent.) of acidity as sulphuric acid, and that neither in the cold nor when heated has dry alcohol any further action on it.

The results quoted for commercial nitre-cake were obtained because the solid, that is, the nitre-cake or partly extracted nitre-cake, was not washed until the washings were neutral. In fact, the above results (table I) show that, with commercial spirits of wine, a neutral washing could not have been obtained until all the acidity had been extracted from the cake.

Preparation of Materials.—Sodium sulphate was prepared by neutralising a solution of pure sodium carbonate with pure sulphuric acid. The solution was evaporated to dryness and fused until neutral.

Sodium hydrogen sulphate, prepared from the calculated quantities of pure sodium carbonate and pure sulphuric acid, was fused at 200° until no further loss was observed. The salt is hygroscopic. It gave the following analysis:

	Found. Per cent.	Calc. Per cent.
Free acid as H_2SO_4	40.76	40.83
Sodium sulphate formed on ignition	59.10	59.18
" SO_4 " as Na_2SO_4	39.80	40.00
" SO_4 " estimated as BaSO_4	67.60	67.53

In all experiments in which pure, dry sodium sulphate of hydrogen sulphate was used, the sulphate was fused and poured into a hot agate mortar, quickly ground up as soon as solidification had set in, and transferred to a weighing bottle.

Sulphuric acid (100 per cent.) was prepared by mixing calculated quantities of pure sulphuric acid with fuming sulphuric acid. The strength was 100.38 per cent., and the concentration was reduced to 100.10 per cent. by exposure to a moist atmosphere.

Ethyl Alcohol.—Pure absolute alcohol was left in contact with lime for several days and then distilled. This operation was repeated until the strength of the distillate, as determined from its density, was 99.80 per cent. by weight.

Alcoholic sulphuric acids were made up by mixing refined alcohol with 100 per cent. sulphuric acid. The approximate strength was obtained by weighing, and the actual strength was determined by titration. Esterification takes place slowly (at 18–19°), and at that temperature about three weeks are required for equilibrium to be established. The percentage "total" acidity, ρ , is found by evaporating a weighed portion of the alcoholic sulphuric acid to pastiness with excess of standard sodium or potassium hydroxide, and then heating in an air-oven for half

an hour at 120°. This ensures complete decomposition of the ethyl hydrogen sulphate. The percentage acidity by direct titration, b , is found by titrating a known weight of the alcoholic sulphuric acid with standard alkali hydroxide. The percentage esterification of the sulphuric acid present is given by

$$\frac{2(a-b)}{a} \times 100.$$

These values (see figure and tables V and VI) have been carefully verified. They differ considerably from those previously available. This work on ethyl hydrogen sulphate will be the subject of a subsequent paper.

Ethyl Ether.—Commercial "pure" ether was dried over calcium chloride, then by exposure to metallic sodium with intermittent shaking, and was finally distilled from sodium.

The Action of Pure, Dry Alcohol on Pure, Dry Sodium Sulphate and its Crystalline Hydrates.

Alcohol has no action on neutral, anhydrous sodium sulphate. Sodium sulphate is sparingly soluble in dilute alcohol.

When the sulphates $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ and $\text{Na}_2\text{SO}_4 \cdot 7\text{H}_2\text{O}$ are treated with dry, cold alcohol, the whole of the water of crystallisation is extracted and the anhydrous sulphate remains. When a supersaturated solution of sodium sulphate in water is treated with warm alcohol (D 0.850), the heptahydrate crystallises out (Löwel, *Ann. Chim. Phys.*, 1851, [iii], **33**, 334; 1857, **49**, 32).

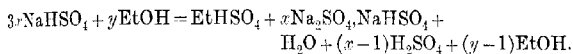
The Action of Pure, Dry Alcohol on Pure, Dry Sodium Hydrogen Sulphate.

The first experiments were carried out with ordinary "absolute" alcohol not specially dried. The dried, powdered hydrogen sulphate was shaken for a short time with excess of this alcohol, filtered, and then washed repeatedly with the same substance. The acidity of the residue fell rapidly to about 18.7 per cent. of sulphuric acid, the washings being strongly acid, and then continued to fall, but very slowly, and the washings were only faintly acid. Two samples, after very exhaustive washing, contained acidities of 17.53 and 17.46 per cent. respectively, and the washings still showed faint acidity. The experiments were repeated with specially dried alcohol prepared as described above, and similar results were obtained. The acidity, as before, rapidly fell to about 18.7 per cent., and then decreased very slowly, but in this

case exhaustive washing reduced the acidity only to 18.07 per cent. and 18.31 per cent. in duplicate samples.

Now, an acidity of 18.7 per cent. corresponds with that of the intermediate sulphate, $\text{Na}_2\text{SO}_4 \cdot \text{NaHSO}_4$, and it was concluded that the rapid reduction of the acidity to approximately this value was due to the formation of this salt. It was further concluded that the reduction of the acidity below 18.7 per cent. was due to water in both cases. The method of extraction on an open filter favoured the absorption of atmospheric moisture by the alcohol.

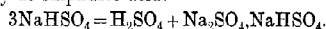
Attempts to eliminate the effect of atmospheric moisture by carrying out the extraction in a Soxhlet apparatus produced similar results; prolonged extraction invariably gave a residue having an acidity slightly below 18.7 per cent. In this case, it was decided that water from another source was responsible, partly, at any rate, for the anomalous results. It has been shown repeatedly in the course of this work that ethyl hydrogen sulphate is invariably formed when alcohol acts on sodium hydrogen sulphate, and it follows that an equivalent quantity of water must be present as a result of this reaction.



In an extraction in a Soxhlet apparatus, this water would dilute the alcohol and would distil over with it, and the effect would be the same as that produced by the undried alcohol in the method of extraction by washing on a filter. Attempts were made to eliminate this water by placing in the flasks of the extraction apparatus (1) anhydrous copper sulphate, and (2) magnesium powder, the latter in the hope that magnesium sulphate and hydrogen would be formed and the production of ethyl hydrogen sulphate prevented. Both failed, owing to the difficulties in carrying out the extraction, caused mainly by violent bumping in the flask. It was finally decided that the best method of attacking the problem was to allow an excess of dried alcohol to remain in contact with the salt for a time sufficient to permit of equilibrium being reached, and then to remove the liquor from the sphere of action as quickly as possible by washing with a neutral solvent. The solvent adopted was ether, dried as described above. A blank experiment, carried out by extracting some dried sodium hydrogen sulphate (acidity, 40.76 per cent.) with the ether in a Soxhlet apparatus, gave, after prolonged extraction, residues containing 40.57 and 40.68 per cent. of sulphuric acid, showing that ether is without action on the hydrogen sulphate. Dried sodium hydrogen sulphate was shaken continuously in a shaking machine with dried alcohol for twenty-four hours, and then filtered off rapidly. The

residue was wrapped in clean paper and extracted in a Soxhlet apparatus with the dried ether until the runnings were neutral. The residue obtained by this method invariably had an acidity lying between 18.66 and 18.74 per cent. of sulphuric acid. Similar results were obtained when the hydrogen sulphate, instead of being shaken with alcohol, was digested with it for several hours under a reflux condenser.

The conclusion is that the action of dry alcohol, either hot or cold, on dry sodium hydrogen sulphate results in the formation of the intermediate sulphate, $\text{Na}_2\text{SO}_4\cdot\text{NaHSO}_4$, containing 18.7 per cent. of acidity as sulphuric acid.



Thus, dry alcohol extracts two-thirds of the acidity from sodium hydrogen sulphate, and the statement found in certain standard works (*loc. cit.*) that sodium hydrogen sulphate is decomposed by alcohol with the formation of neutral sulphate, requires revision. Complete extraction of the acid only takes place when the alcohol is contaminated with water.

The action of alcohol on potassium hydrogen sulphate was next examined. The "pure" material was fused until no further loss of weight could be detected. The acidity was 36.15 per cent. (calc.: 36.03 per cent.). Several samples were treated with alcohol and extracted with ether, as in the case of the sodium salt, and the acidity in the residue was estimated. In all the samples the acidity lay between 35.59 and 35.84 per cent. It is thus evident that the decomposition of potassium hydrogen sulphate by dry alcohol is negligible. This result is recorded independently by Borntraeger (*Annali Chim. Appl.*, 1919, 12, 1).

The action of several other aliphatic alcohols on sodium hydrogen sulphate was examined to see if their behaviour is similar to that of ethyl alcohol. The results are given in table II.

TABLE II.

Action of certain Aliphatic Alcohols on Dry Sodium Hydrogen Sulphate.

Alcohol.	Boiling point under 610 mm. pressure.*	Acidity of residue. Per cent.
Methyl alcohol	59.5°	18.68
Ethyl alcohol	72.5°	18.68
n-Butyl alcohol	110-111°	18.65
Amyl alcohol	125.0°	18.66

* Normal pressure at the laboratory at which the work was done.

The Nature of the Reaction between Alcohol and Sodium Hydrogen Sulphate.

During the investigation of the reaction by repeated washings with alcohol on a filter, the washings were collected and the acidity was determined by titration. It was noticed that the acid found in the washings was always less than that which had disappeared from the salt. It was suspected that this discrepancy was due to the formation of ethyl hydrogen sulphate. The liquors were examined for this substance, and its presence was confirmed.

The method of analysis employed for determining in these alcoholic extracts both the total acidity and the extent of conversion into ethyl hydrogen sulphate is that described above under "alcoholic sulphuric acids."

The question then arose: Is the ethyl hydrogen sulphate formed as a result of direct action between the alcohol and the hydrogen sulphate, or is its formation a secondary reaction between the alcohol present and the sulphuric acid extracted directly from the hydrogen sulphate?

The solution of the problem involved an examination of the reaction occurring when dry alcohol and dry sulphuric acid are mixed in varying proportions. The detailed results of this examination will be given in a separate paper, and it is sufficient to state here that:

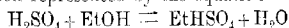
(1) At the ordinary temperature (18° to 19°) equilibrium between the product, ethyl hydrogen sulphate, and the reacting substances is reached very slowly, and requires about two or three weeks for completion.

(2) The extent of the conversion depends on the proportions in which the reacting substances are present.

The curve indicates the percentage esterification of the total sulphuric acid present for varying proportions of alcohol and sulphuric acid after equilibrium has been attained.

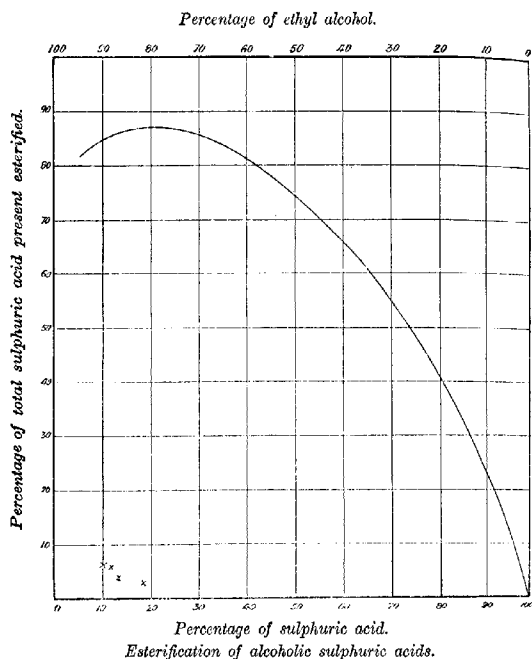
The answer to the question proposed was found by a comparison of results obtained with acid alcoholic liquids prepared from sodium hydrogen sulphate with the values on the above curve.

Since the action represented by the equation



takes some time to reach equilibrium, it follows that, if the presence of ethyl hydrogen sulphate in the liquor prepared from sodium hydrogen sulphate is due to this reaction, the examination of such liquors immediately after the substances have been shaken together should show percentage conversion lower than those on the above curve. If, on the other hand, the ethyl hydrogen sulphate is pro-

duced as a result of direct action between the alcohol and the hydrogen sulphate, the value should lie either on its curve or above it, according as the reaction $\text{EtHSO}_4 + \text{H}_2\text{O} \rightarrow \text{EtOH} + \text{H}_2\text{SO}_4$ reaches equilibrium quickly or slowly. (The velocity of this reaction was not studied quantitatively during this work, but it has been observed that the hydrolysis takes place slowly.) Quantities



of sodium hydrogen sulphate and alcohol in varying proportions were shaken for twenty-four hours and filtered. Table III (p. 657) shows the degree of conversion of the sulphuric acid in the filtrate into ethyl hydrogen sulphate.

The values in the fifth column lie far below those on the curve, and it appears, therefore, that the formation of ethyl hydrogen sulphate is a secondary reaction between alcohol and sulphuric acid, the latter being produced as the result of a primary reaction between alcohol and hydrogen sulphate. It has not been found possible to ascertain the precise nature of this primary reaction.

Experiments were performed in order to ascertain whether the

TABLE III.

Sodium hydrogen sulphate. Grams.	Ethyl alcohol. Grams.	Acidity of filtrate as percentage of sulphuric acid.		Esterifica- tion. Per cent.	Acid ex- tracted. Theory = 2.72 grams. Grams.
		By direct titration.	Total.		
10	12	18.12	18.31	2.07	2.69
10	12	18.44	18.73	3.10	2.77
10	18	12.90	13.10	3.05	2.71
10	21	10.99	11.30	5.48	2.68
10	24	9.70	9.98	5.61	2.66
10	24	9.74	10.04	5.97	2.68

process of extraction of the acid is practically instantaneous or whether it takes some time. The results are shown in table IV, from which it will be seen that the extraction is rapid, but not instantaneous. Powdered sodium hydrogen sulphate was vigorously shaken with alcohol for the time shown in the third column. As the time of shaking increased, the mixture became more viscous. The actual time allowed for filtration is shown in the fourth column. The total quantity of acid extracted from the 5 grams of hydrogen sulphate was calculated from the acidity of the filtrate. The tests, although not of a high degree of accuracy, are sufficiently conclusive to give the desired information.

TABLE IV.

Estimation of the Rate of Extraction of Sulphuric Acid from Sodium Hydrogen Sulphate by means of Alcohol.

Sodium hydro- gen sul- phate. Grams.	Alcohol. Grams.	Time dur- ing which the mix- ture was shaken.	Time allowed for filtra- tion.	Weight of filtrate. Grams.	Percent- age of acid in filtrate. Theory	Weight of acid actu- ally re- covered. Grams. Theory
		Minutes.	Minutes.		8.8.	1.36.
5	14.1	1.0	0.75	6.097	5.07	0.75
5	14.0	2.0	1.0	2.925	6.97	1.06
5	14.0	4.0	2.0	2.188	8.02	1.22
5	14.0	8.0	3.0	1.981	8.27 8.39	1.24 1.28

The maximum amount of extraction shown in this table amounts to 94.1 per cent. of that theoretically possible. From the last column of table III, it will be seen that when the extraction is continued for twenty-four hours, the acid extracted from the sodium hydrogen sulphate agrees with that demanded by theory, assuming the quantitative conversion of the sodium hydrogen sulphate into the compound $\text{Na}_2\text{SO}_4, \text{NaHSO}_4$. Subsequent investigation showed that extraction for two hours is more than sufficient to ensure the completion of this reaction.

The Action of Alcoholic Sulphuric Acid on Pure, Dry Sodium Sulphate.

Powdered sodium sulphate was mixed with more than twice its weight of alcoholic sulphuric acid, shaken for seventy-two hours, and then filtered off. The acid in the filtrate was determined as in the alcoholic sulphuric acids. The salt was quickly removed from the filter, wrapped in clean paper, and extracted by means of ether in a Soxhlet apparatus until the runnings were neutral. During the shaking, all mixtures become more or less gelatinous. The time during which the extraction lasted is given in the second column of table V. The figure in brackets indicates the number of hours of that time during which the continuous extraction in the Soxhlet apparatus was proceeding. For the rest of the time the substance was lying immersed in the ether. The times only give an approximate idea of the time taken for extraction, as, owing to the difficulty of judging the end-point, it is probable that some samples were left exposed to the action of the ether longer than was absolutely necessary. The two results shown under Nos. 6 and 7 in table V illustrate the considerable length of time required in these cases to complete the reaction.

TABLE V.

Action of Alcoholic Sulphuric Acid on Dry Sodium Sulphate.

No.	Time extracted.	Percent- age of acid in the alco- holic sulphuric acid.	Percentage con- version into ethyl hydrogen sulphate of constituents.		Acidity in residue as per- centage of sul- phuric acid.	Notes.
			Acid.	Alcohol.		
1	6½ days (20)	9.19	82.5	3.9	0.57	
2	—	20.41	87.7	10.6	1.53	
3	8½ days (36)	29.9	83.7	17.5	5.83	
4	9 days (41)	40.6	81.0	26.2	10.83	
5	9 days (41)	50.6	72.5	34.0	12.49	
6	11 days (53)	70.2	54.5	60.4	19.98	incomplete.
	18 days (102)	70.2	54.5	60.4	18.80	neutral washings.
7	15 days (65)	78.8	41.0	71.5	27.69	incomplete
	23 days (117)	78.8	41.0	71.5	18.59	neutral washings.

From these results it will be observed that sodium sulphate combines with sulphuric acid presented to it as alcoholic sulphuric acid. The amount of combination increases with the strength of the alcoholic sulphuric acid used, but is not directly proportional to it. The table gives the results after the sodium sulphate had

been left in contact with the alcoholic sulphuric acid for seventy-two hours with constant shaking. Owing to pressure of work, it was not possible to examine the influence of time on the action of alcoholic sulphuric acids on sodium sulphate.*

The Action of Alcoholic Sulphuric Acid on Dry Sodium Hydrogen Sulphate.

Sodium hydrogen sulphate was mixed with about six times its weight of alcoholic sulphuric acid and shaken for twenty-four hours. The solid was then filtered off, wrapped in clean paper, and placed in a Soxhlet apparatus for extraction with dry ether. The acidity of the residue in the paper was estimated as soon as the runnings from the apparatus were neutral. The observed results are given in table VI.

TABLE VI.

Action of Alcoholic Sulphuric Acid on Dry Sodium Hydrogen Sulphate.

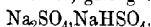
No.	No. of hours extracted.	Strength of alcoholic sulphuric acid as percentage of sulphuric acid.	Percentage conversion of constituents into ethyl hydrogen sulphate.		As percentage of sulphuric acid.	
			Acid.	Alcohol.	Acidity in filtrate after shaking.	Acidity of residue
1	13	9.1	82.5	3.0	13.5	18.83
2	34	21.6	87.1	11.3	28.8	18.64
3	38	29.9	83.7	17.5	32.9	26.31
4	82	40.6	81.0	26.2	39.1	27.69
5	38	50.6	72.5	34.0	50.1	23.62
	?	50.6	72.5	34.0	50.1	18.93
6	34	60.6	64.5	44.5	57.5	33.60
	74	60.6	64.5	44.5	57.5	18.63
7	50	70.2	54.5	60.4	67.8	27.86
8	86	78.8	41.0	71.5	78.1	23.63

* It is necessary to exercise great care in testing the runnings with litmus paper as, when the acid is small in quantity, its presence is not indicated until all the ether has evaporated from the paper.

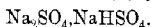
In the cases of specimens treated with alcoholic sulphuric acids of the higher acid-contents, it was observed that the liquor in the flask of the Soxhlet apparatus separated into two layers. This was due to the presence of ethyl hydrogen sulphate. This substance was also found in washings in which no separation into layers had occurred. The solubility of ethyl hydrogen sulphate in ether is less than one per cent., and consequently, if there is much ethyl hydrogen sulphate present, it shows itself by causing the appearance of two layers in the flask.

These remarks apply also to the next section.

From these figures it is evident that alcoholic sulphuric acid reacts with sodium hydrogen sulphate. It appears that alcoholic sulphuric acids of which the strength is about 20 per cent. and less extract acid from the hydrogen sulphate and leave a residue of the compound $\text{Na}_2\text{SO}_4, \text{NaHSO}_4$, whilst acids of 30 per cent. and more also react with the hydrogen sulphate and give another sulphate of sodium, which has previously been prepared by a different method, having the formula $\text{Na}_2\text{SO}_4, 2\text{NaHSO}_4$ and an acidity of 25.65 per cent. The formation of this compound has not been definitely proved, but, if it is formed, it is decomposed by exhaustive extraction with ether, giving the compound



The mixtures of alcoholic sulphuric acid and sodium hydrogen sulphate become gelatinous during the shaking, and, if the substance in the Soxhlet apparatus is examined during the extraction, crystals of considerable size are found. These crystals seem to be formed in the bottle or during the extraction, for the hydrogen sulphate was always carefully powdered before exposing it to the action of the alcoholic sulphuric acid. The crystals probably consist of the compound $\text{Na}_2\text{SO}_4, 2\text{NaHSO}_4$, as they are not observed when the product of the extraction is the compound



The extraction was fairly rapid at first, and the litmus with which the runnings were tested showed a bright pink coloration. After some time the extraction became very slow, and the acidity towards litmus paper was obvious, but extremely weak (see footnote, p. 659). This will explain the various times shown in the table for extraction; for example, one sample, after actual extraction for eighty-two hours and remaining in ether for the remainder of a fortnight when the extraction was not proceeding, showed an acidity of 27.7 per cent. The remainder of the sample was then replaced and was extracted for twenty-four hours more, and when not under continuous extraction was left in the dry ether, the whole experiment lasting about three days. After this treatment the acidity was 24.7 per cent. As a comparison, it may be stated that the ethereal extraction of sodium hydrogen sulphate, after treatment with alcohol, takes only a few hours to complete.

It will be observed that the acidity of the filtrates in cases 1, 2, and 3 is greater than the original acidity of the alcoholic sulphuric acid; in all other cases it is about the same or a little less.

to it.

Discussion of certain Properties of the Intermediate Sulphate,
 $\text{Na}_2\text{SO}_4 \cdot \text{NaHSO}_4$.

The compound, $\text{Na}_2\text{SO}_4 \cdot \text{NaHSO}_4$, which is so readily formed by the action of dry alcohol on dry sodium hydrogen sulphate, is dealt with by Pascal and Ero (*loc. cit.*), although the substance was prepared by a different method from that described in this paper. In the course of the present work it has been necessary to study this compound in some detail, and the results do not confirm the observations of Pascal and Ero, who state that the intermediate sulphate decomposes at 174° with partial liquefaction. Specimens of the intermediate sulphate, $\text{Na}_2\text{SO}_4 \cdot \text{NaHSO}_4$, were prepared by extraction of sodium sulphate by alcohol, and the statement that the substance is unchanged in air was confirmed. The acidity of the different samples ranged from 18.66 to 18.78 per cent. A weighed quantity of the substance was then heated in a platinum basin in an oil-oven, and cooled and weighed at intervals. The temperature of the bath was raised about 4° or 5° at a time until the temperature reached 215° . The salt was kept in the bath for about half an hour at each temperature, and weighed after each heating. It showed no signs of melting, and its weight was constant. Over the whole period of a particular experiment, 7.3038 grams of the substance lost 0.0254 gram. The acidity at the commencement of the experiment was 18.67 per cent., and the acidity after the prolonged heating was 18.74 per cent. This result has been frequently confirmed. The only difference in the substance after heating was that the colour had changed to a pale grey. The salt as prepared is snow-white. Every attempt on the part of the authors to determine the melting point resulted in failure. Even when heated to 260° the substance did not melt. It seemed possible that Pascal and Ero, having prepared their specimens from solutions, might have determined the melting point of a substance containing water, and that the presence of water would cause it to melt. A sample of the intermediate sulphate was prepared by the recrystallisation of nitre-cake (33 per cent. of sulphuric acid), and gave the following analysis:

	I.	II.	III.
	Found.	Calculated	
	Per cent.	from I, assum- ing the salt dehydrated.	Theory for the dry salt.
Acidity as H_2SO_4	18.45 } 18.50 }	19.28	18.70
SO_4 determined as BaSO_4	70.58	73.41	73.29
Na_2SO_4 produced on fusion ...	77.42 } 77.43 }	80.69	81.30
Water	3.95 } 4.02 }	—	—

The salt obtained by recrystallisation contained a slight excess of acid above that required for the intermediate compound. On heating, water was given off, but fusion did not take place. The authors are unable to account for the observations quoted in the paper mentioned (*loc. cit.*). The substance, $\text{Na}_2\text{SO}_4 \cdot \text{NaHSO}_4$, decomposes before it melts, the residue after heating being fused sodium sulphate.

The Action of Pure, Dry Alcohol on Mixtures of Pure, Dry Sodium Sulphate and Pure, Dry Sodium Hydrogen Sulphate before and after Heating the Mixtures.

The next series of experiments was carried out with the object of elucidating the composition of commercial nitre-cake. It is usually assumed that nitre-cake is a mixture of sodium hydrogen sulphate and sodium sulphate, but recently Pascal and Ero (*loc. cit.*) have stated that, at the ordinary temperature, it is a mixture of the intermediate sulphate, $\text{Na}_2\text{SO}_4 \cdot \text{NaHSO}_4$, and the hydrogen sulphate. Pascal and Ero's statement is based on a study of the melting points of mixtures of neutral sulphate and sulphuric acid, and their conclusions are not therefore necessarily applicable to nitre-cake. It occurred to the authors that a study of the action of alcohol on (1) mixtures of sodium sulphate and hydrogen sulphate, and (2) commercial nitre-cake, would probably throw light on the subject, and experiments were accordingly carried out on these lines. As a preliminary experiment, it was necessary to ascertain if there is any evolution of sulphuric acid from such mixtures when heated to 215° , as the conclusions drawn depend on the assumption that, before extraction with alcohol, the total amount of acid in the mixture is the same as the amount of acidity in the mixture when weighed out for the experiment. Results show that mixtures of sodium sulphate and sodium hydrogen sulphate do not lose sulphuric acid when heated to 215° .

(a) *Table VII. Nos. 1 to 7.*—Dry sodium sulphate and dry sodium hydrogen sulphate were shaken with excess of alcohol for twenty-four hours. The solid was then filtered off and extracted with dry ether until the runnings were neutral.

(b) *Table VII. Nos. 8 to 13.*—In all these cases the salts were treated as above, except that, before the alcohol extraction, the mixed salts were heated in an oil-oven for four hours at 200 – 215° . In No. 13 the mixture was heated for six and a-half hours to see if the reaction became quantitative if given sufficient time. The analyses indicate that the reaction was complete in the shorter time, namely, **four hours**.

The values shown in column vii are found by calculation, assuming that all the sodium hydrogen sulphate is converted into the compound, $\text{Na}_2\text{SO}_4 \cdot \text{NaHSO}_4$, and that as much sodium sulphate as possible combines with the sulphuric acid so liberated, also forming the compound, $\text{Na}_2\text{SO}_4 \cdot \text{NaHSO}_4$.

It will be seen that, in every case, the acidity of the residue is greater than it would be if the hydrogen sulphate only took part in the reaction (column iv), but less than the value shown in column vii. Participation of the sodium sulphate in the reaction is indicated in every case, although (see column viii) its conversion into the compound, $\text{Na}_2\text{SO}_4 \cdot \text{NaHSO}_4$, is never complete.

Two explanations are possible of the part taken by the sodium sulphate in the reaction:

(1) That, in the presence of alcohol, some of the sulphate combines directly with the sodium hydrogen sulphate. No evidence in favour of this possibility has been found.

(2) That the alcoholic sulphuric acid produced by the action of the alcohol on the sodium hydrogen sulphate reacts with a portion of the sulphate, forming the compound, $\text{Na}_2\text{SO}_4 \cdot \text{NaHSO}_4$.

Sulphuric acid acts on sodium sulphate in the presence of water, and it seemed not unlikely that it might act on sodium sulphate in the presence of alcohol. This point was thoroughly investigated, and the results obtained (p. 658) show conclusively that (a) anhydrous sodium sulphate is acted on by alcoholic sulphuric acid at the ordinary temperature, and (b) that the amount of interaction increases with the strength of alcoholic sulphuric acid employed.

In the second series of analyses, obtained in experiments in which the substances under consideration were heated, it will be seen that the heating of the two salts in contact results in a very considerable formation of the compound, $\text{Na}_2\text{SO}_4 \cdot \text{NaHSO}_4$, as indicated by the increased acidity of the residue after extraction (see table VII, columns v to viii, and compare Nos. 8 to 13 with Nos. 1 to 7). The mixtures (except No. 13) were heated for four hours at 200–215°. Prolonged heating does not increase the yield of intermediate sulphate. Considering the difficulties of complete admixture and the fact that the mixtures never completely fused, the results lead one to expect a still higher conversion to the compound under ideal conditions. It appears that if the ratio $\text{Na}_2\text{SO}_4 : \text{NaHSO}_4$ is greater than unity, the degree of conversion to the double compound is greater than when the ratio $\text{NaHSO}_4 : \text{Na}_2\text{SO}_4$ is greater than unity.

TABLE VII.
*Action of Pure, Dry Alcohol on Mixtures of Sodium Sulphate and Sodium Hydrogen Sulphate
 both before and after Heating.*

Mixtures of sodium sulphate and sodium hydrogen sulphate not heated after mixing.

Expt. No.	Composition of mixture.		Corresponding with approximate molecular proportions.	Initial acidity of mixture.		Acidity of residue. Per cent. H ₂ SO ₄ .	Calculated acid- ity of residue assuming com- plete conversion of NaHSO ₄ into Na ₂ H(SO ₄) ₂ , the Na ₂ SO ₄ remain- ing unaffected. Per cent. H ₂ SO ₄ .	Calculated acid- ity of residue assuming maxi- mum possible conversion of both NaHSO ₄ and Na ₂ SO ₄ into the compound Na ₂ H(SO ₄) ₂ . Per cent. H ₂ SO ₄ .	Conversion of Na ₂ SO ₄ into Na ₂ H(SO ₄) ₂ ex- pressed as the percentage of the total Na ₂ SO ₄ originally present which could have been so con- verted.
	Na ₂ SO ₄ . Per cent.	NaHSO ₄ . Per cent.		Per cent. H ₂ SO ₄ .	Per cent. H ₂ SO ₄ .				
1	70.3	29.7	2Na ₂ SO ₄ : NaHSO ₄ ...	12.1	7.74	4.40	12.1	12.1	43.4
2	54.2	45.8	Na ₂ SO ₄ : NaHSO ₄ ...	18.7	9.88	7.08	18.7	18.7	23.9
3	37.2	62.8	Na ₂ SO ₄ : 2NaHSO ₄ ...	25.6	13.20	10.31	18.7	18.7	34.5
4	20.0	80.0	Na ₂ SO ₄ : 4.7NaHSO ₄	32.6	17.31	13.92	18.7	18.7	71.0
5	17.0	83.0	Composition of nitre- cake if it were a mix- ture of Na ₂ SO ₄ and NaHSO ₄ .	33.8	15.98	14.59	18.7	18.7	33.6
6	8.6	91.4	Approximately Na ₂ SO ₄ : 13NaHSO ₄ .	37.3	17.16	16.57	18.7	18.7	26.6
7	0.0	100.0	NaHSO ₄	40.8	18.09	18.70	18.7	18.7	—

Mixtures of sodium sulphate and sodium hydrogen sulphate heated at 200—215° after pulverisation and intimate mixing.

8	70.3	29.7	2Na ₂ SO ₄ :NaHSO ₄ ...	12.1	11.50	4.40	12.1	92.2
9	64.8	35.2	3Na ₂ SO ₄ :2NaHSO ₄ ...	14.4	14.85	5.30	15.2	96.3
10	54.2	45.8	Na ₂ SO ₄ :NaHSO ₄ ...	18.7	15.71	7.08	18.7	74.2
11	37.2	62.8	Na ₂ SO ₄ :2NaHSO ₄ ...	25.6	17.01	10.31	18.7	80.6
12	29.7	70.3	Na ₂ SO ₄ :3NaHSO ₄ ...	28.7	17.29	11.84	18.7	79.5
13	37.2	62.8	Na ₂ SO ₄ :2NaHSO ₄ ...	25.6	16.94	10.31	18.7	79.0
								Mixture heated 6½ hours.

Substances prepared from sodium nitrate and sulphuric acid, that is, nitre-cakes.

14	17.0	83.0	Nitre-cake from fac- tory retort.	33.8	18.78	14.59	18.7	100.0
15	54.2	45.8	Nitre-cake prepared in laboratory to give molecular proportions. Na ₂ SO ₄ :NaHSO ₄ .	19.0	18.58	7.08	18.7	99.0
16	70.6	29.4	Nitre-cake prepared in laboratory.	12.0	11.96	4.35	12.00	—
Col.	i.	ii.	iii.	iv.	v.	vi.	vii.	viii.

Constitution of Nitre-cake.

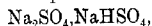
The results given in table VII provide conclusive evidence regarding the constitution of nitre-cake. It will be noticed from experiments Nos. 14, 15, and 16 that:

(a) When the original acidity of the cake is more than 18.7 per cent., extraction with dry alcohol reduces it to 18.7 per cent., indicating a complete conversion of the sodium hydrogen sulphate present in the cake into the compound, $\text{Na}_2\text{SO}_4\cdot\text{NaHSO}_4$.

(b) When the original acidity of the cake is about 18.7 per cent., treatment with dry alcohol leaves it unaltered.

(c) When the original acidity of the cake is less than 18.7 per cent., treatment with dry alcohol again leaves it unaltered.

Experiments 1 to 6 having shown that when mixtures of sodium sulphate and sodium hydrogen sulphate are extracted with alcohol the sodium sulphate is never completely converted into the compound, $\text{Na}_2\text{SO}_4\cdot\text{NaHSO}_4$, it follows from the above results that nitre-cakes of 18.7 per cent. acidity and more contain no sodium sulphate at all. Cakes of more than 18.7 per cent. acidity consist of a mixture of sodium hydrogen sulphate and the compound, $\text{Na}_2\text{SO}_4\cdot\text{NaHSO}_4$, and cakes of less than 18.7 per cent. acidity comprise a mixture of sodium sulphate and the compound,



containing no hydrogen sulphate at all, for, if hydrogen sulphate were present, extraction with alcohol would reduce the acidity. Finally, a cake of 18.7 per cent. acidity consists of the compound, $\text{Na}_2\text{SO}_4\cdot\text{NaHSO}_4$, and contains neither sulphate nor hydrogen sulphate.

The molecular proportions of a nitre-cake of known acidity may be calculated from one of the two formulæ given below:

(a) If the acidity of the nitre-cake is 18.7 per cent. sulphuric acid or less, $x = 1 - \frac{142y}{4900 - 120y}$, where x = the molecular proportion of sodium sulphate, $(1-x)$ = the molecular proportion of the compound, $\text{Na}_2\text{SO}_4\cdot\text{NaHSO}_4$, in the cake, and y = its acidity as percentage of sulphuric acid.

(b) If the acidity is 18.7 per cent. of sulphuric acid, or more, but not exceeding 40.83 per cent., $x = \frac{4900 - 120y}{142y}$, where x = the molecular proportion of the compound, $\text{Na}_2\text{SO}_4\cdot\text{NaHSO}_4$, $(1-x)$ = the molecular proportion of sodium hydrogen sulphate in the nitre cake, and y = its acidity as percentage of sulphuric acid.

Summary and Conclusions.

(1) Dry alcohol acts on dry sodium hydrogen sulphate, with the formation of the intermediate sulphate, $\text{Na}_2\text{SO}_4, \text{NaHSO}_4$, and the liberation of sulphuric acid, which dissolves in the alcohol, and is subsequently converted partly into ethyl hydrogen sulphate. Prolonged action of alcohol does not extract any further quantity of the acid.

(2) Methyl, *n*-butyl, and amyl alcohols also react with sodium hydrogen sulphate, with the formation of the same intermediate sulphate.

(3) Dry ethyl alcohol does not decompose dry potassium hydrogen sulphate.

(4) Moist alcohol will completely decompose sodium hydrogen sulphate, giving first the intermediate sulphate, $\text{Na}_2\text{SO}_4, \text{NaHSO}_4$, and finally normal sodium sulphate. Sodium sulphate is sparingly soluble in moist alcohol.

(5) Alcoholic sulphuric acid reacts with sodium sulphate in the cold (18°), with the formation of an acid sulphate. The amount of the interaction increases with the strength of the alcoholic sulphuric acid employed.

(6) When alcoholic sulphuric acid acts on sodium hydrogen sulphate, the intermediate sulphate, $\text{Na}_2\text{SO}_4, \text{NaHSO}_4$, is formed if the strength of the alcoholic sulphuric acid corresponds with 20 per cent. or less. When the alcoholic sulphuric acid has a strength corresponding with 30 per cent. of sulphuric acid or more, the compound, $\text{Na}_2\text{SO}_4, 2\text{NaHSO}_4$, is probably produced; if so, this compound is slowly decomposed by constant extraction with pure, dry ether, and finally yields the compound, $\text{Na}_2\text{SO}_4, \text{NaHSO}_4$.

(7) The compound, $\text{Na}_2\text{SO}_4, \text{NaHSO}_4$, is formed when dry sodium sulphate is heated with dry sodium hydrogen sulphate.

(8) Nitre-cake consists of the compound $\text{Na}_2\text{SO}_4, \text{NaHSO}_4$, alone or mixed with either sodium hydrogen sulphate or sodium sulphate, according as the acidity is equal to, greater than, or less than 18.7 per cent. of sulphuric acid.

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THE CHEMICAL LABORATORY,
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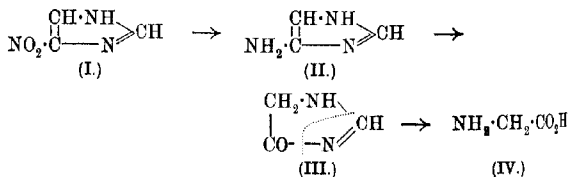
ARUVANKADU, S. INDIA.

[Received, December 30th, 1919.]

LXX.—*Orientation of the Nitro- and Arylazo-glyoxalines. Fission of the Glyoxalone Nucleus.*

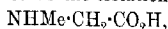
By ROBERT GEORGE FARGHER.

IN the course of a recent communication (T., 1919, 115, 217), the author, in conjunction with Prof. F. L. Pyman, showed that the nitro-group, on entering the glyoxaline nucleus, takes up the 4- or 5-position.* Subsequent reduction with tin and hydrochloric acid, undertaken with the object of examining the corresponding amino-glyoxalines and determining directly the orientation of the nitro-group, led to fission of the nucleus, two of the three nitrogen atoms appearing in the form of ammonia. It was suggested that the first stage of the disintegration was probably the elimination of the amino-group as ammonia with formation of a glyoxalone, certain members of the purine group—also derivatives of 4-amino-glyoxaline—having been shown to undergo hydrolysis in this manner (compare Tafel and Meyer, *Ber.*, 1908, 41, 2546; Biltz, *Ber.*, 1910, 43, 1589). It was therefore of interest to investigate the reduction in more detail with the objects (1) of determining directly the orientation of the nitro-group, (2) of establishing the transformation into the glyoxalone, and (3) of studying the fission of the simple glyoxalone nucleus under the influence of acids. The earlier experiments had shown that the products of complete reduction, apart from ammonium chloride, the predominant constituent, were very uninviting in appearance. Consequently, treatment in cold hydrochloric acid solution with just sufficient stannous chloride to reduce the nitro-group was employed, with success. Nitro-glyoxaline, in addition to ammonia, yielded glycine, as did also nitro-2-methylglyoxaline, whilst nitro-5-methylglyoxaline yielded α -alanine. This clearly demonstrates that the nitroglyoxalines are correctly formulated as 4-nitro-derivatives, that the reduction is followed by hydrolysis of the 4-aminoglyoxaline (II), with the



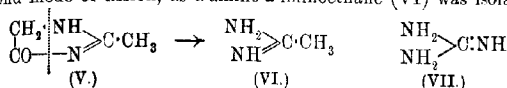
* In glyoxalines containing a free imino-group the 4- and 5-positions are equivalent.

formation of the 4-glyoxalone (III), and that one fission of the 4-glyoxalone nucleus takes place between the 1:2- and 3:4-positions. This fission recalls the isolation of sarcosine,



by Rosengarten and Strecker (*Annalen*, 1871, **157**, 1) as a product of hydrolysis of caffeine by baryta.

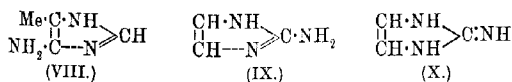
The reduction of nitro-2-methylglyoxaline gave evidence of a second mode of fission, as α -amino- α -iminoethane (VI) was isolated.



Fission therefore takes place between the 1:5- and 3:4-positions (V), presumably with simultaneous formation of glycollic acid, and reveals the probable mechanism of the formation of guanidine (VII) in the reduction of 2-benzeneazoglyoxaline.

What is practically the reverse process was accomplished by Finger (*J. pr. Chem.*, 1907, [ii], **76**, 93), who condensed α -imino-ethoxyethane with the ethyl ester of glycine, and obtained methyl-4-glyoxalone.

In neither of these reductions was the aminoglyoxaline obtained. Consequently, the isolation of a small and variable proportion of α -amino-5-methylglyoxaline (VIII) from the reduction of 4-nitro-methylglyoxaline was both unexpected and important, and permitted comparison of a simple 4-aminoglyoxaline with the 2-aminoglyoxaline isolated in the earlier work (*loc. cit.*, pp. 223, 246). It was already evident that they evinced a considerable difference in stability, and the dissimilarity extends to most of the other properties. Whilst 2-aminoglyoxaline (IX) is a monacidic base, which does not yield a benzylidene derivative, does not react with sodium- β -naphthoxide after treatment with nitrous acid,* and, in brief, behaves in many of its reactions as if it existed in the tautomeric form (X), 4-amino-5-methylglyoxaline reacts as a true aromatic amine, forming a *dihydrochloride* and a crystalline *benzylidene* derivative, and coupling readily with sodium- β -naphthoxide after treatment with nitrous acid.



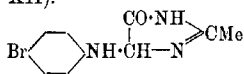
In the previous communication it was also shown that the aryl-glyoxalines were true *C*-azo-, and not *N*-azo-, compounds, as had

* I am indebted to Prof. Pyman, who has, since the appearance of our joint communication, made a further study of the 2-aminoglyoxalines, for his correction (compare *loc. cit.*, p. 243).

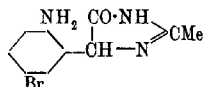
been suggested by Rung and Behrend (*Annalen*, 1892, **271**, 28) and Burian (*Ber.*, 1904, **37**, 696). Whilst, however, in the case of the 2-arylazoglyoxalines this was established by a study of their reduction products, proof of the constitution of the 4-arylazo-derivatives was mainly indirect. On complete reduction, they behaved like the nitroglyoxalines, the ring undergoing fission, whilst their general properties were antagonistic to the supposition that they were 1-arylazo-derivatives.

As the results now obtained with the nitroglyoxalines indicated the course the reaction might be expected to take, it was evident that the formation of glyoxalone derivatives in the reduction of the 4-arylazoglyoxalines would definitely determine the orientation of the arylazo-group.

The reduction of *p*-bromobenzeneazo-2-methylglyoxaline and 4-benzeneazo-5-methylglyoxaline was therefore undertaken under the same conditions as had been successful in the case of the nitroglyoxalines. The former, which, previously, had yielded only *p*-bromoaniline and ammonia as isolable reduction products, readily gave a *glyoxalone*, for which there were two possible formulæ (XI, XII).

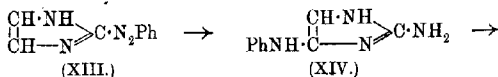


(XI.)



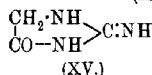
(XII.)

The formation of a *benzylidene* derivative similar to that obtained from 2-amino-4-*p*-aminophenylglyoxaline shows the second of these to be correct. The failure, therefore, of the compound to give more than a faint yellow colour with sodium- β -naphthoxide after treatment with nitrous acid is interesting. The comparative stability towards hydrochloric acid serves to confirm the constitution, as an earlier stage in the formation of glycoeyamidine (XV) and alacreatinine from 2-benzeneazoglyoxaline (XIII) and 2-benzeneazo-5-methylglyoxaline respectively, by reduction with zinc and acetic acid, is no doubt represented by 2-amino-4-anilino-glyoxaline (XIV) and 2-amino-4-anilino-5-methylglyoxaline, which then undergo hydrolysis and rearrangement.



(XIII.)

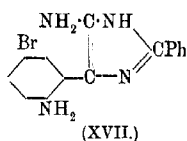
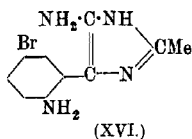
(XIV.)



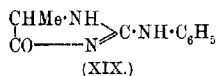
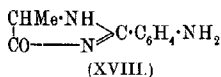
(XV.)

Practically the whole of the reduction product appeared in the

form of an insoluble stannichloride, probably that of 5-amino-4-(2'-amino-5'-bromophenyl)-2-methylglyoxaline (XVI), as, after

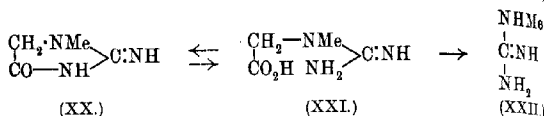


conversion into the hydrochloride, roughly molecular proportions of ammonium chloride and the glyoxalone were obtained on fractionation. It is therefore permissible to assume that the constitution of the reduction product of bromobenzeneazo-2-phenylglyoxaline (*loc. cit.*, p. 258) is correctly represented as 5-amino-4-(2'-amino-5'-bromophenyl)-2-phenylglyoxaline (XVII), the product evincing a greater stability towards acids than the corresponding 2-methyl derivative. The further study of the reduction of 4-benzeneazo-5-methylglyoxaline was of interest, as two products of undetermined constitution had already been isolated, a base, $\text{C}_9\text{H}_{10}\text{ON}_2$, from the reduction with tin and hydrochloric acid (*loc. cit.*, p. 254), and a base, $\text{C}_{10}\text{H}_{11}\text{ON}_3$, from the reduction with zinc and acetic acid (*loc. cit.*, p. 255). The reduction with cold stannous chloride has now yielded, in addition to the base, $\text{C}_9\text{H}_{10}\text{ON}_2$, a third compound, $\text{C}_{10}\text{H}_{11}\text{ON}_3$, not identical with the product of the zinc reduction. It gave a *dihydrochloride*, a *benzylidene* derivative, and, after treatment with nitrous acid, coupled with sodium- β -naphthoxide, and is therefore 2-p-amino-phenacyl-5-methyl-4-glyoxalone (XVIII).



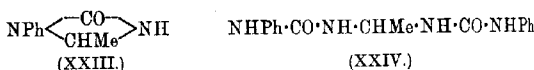
The base from the zinc reduction was monacidic, did not couple, and did not react with benzaldehyde, and is therefore 2-anilino-5-methyl-4-glyoxalone (XIX). It is of interest to record that the reactions which have been examined so far indicate that the zinc and acetic acid reduction favours the semidine change, whilst the stannous chloride reduction favours the benzidine change. It does not follow, however, that the reaction proceeds entirely in the one direction, as, for example, a small proportion of 2-5'-bromo-2'-aminoanilino-glyoxaline (*loc. cit.*, p. 246) is produced in the reduction of 2-p-bromobenzeneazoglyoxaline, whilst the guanidine formed in the reduction of 2-benzeneazoglyoxaline conceivably originates from 2-amino-4-anilino-glyoxaline through the intermediate formation of glycocyamidine. This is of interest in view of the close

relationship of creatine (XXI) to creatinine (XX) and the suggestion that the former is the precursor of methylguanidine (XXII)



in the organism (Achelis, *Zeitsch. physiol. Chem.*, 1906, 50, 10).

Neither of the modes of fission established in the simple glyoxal-one nucleus accounts for the formation of the base, $\text{C}_9\text{H}_{10}\text{ON}_2$, from either 2-*p*-aminophenyl-5-methyl-4-glyoxal-3-one or 2-anilino-5-methyl-4-glyoxal-3-one, one of which probably represents an earlier stage in its formation. It is difficult to avoid the supposition that fission ensues between the 4:5- and 2:3-positions, the reaction being conditioned by the presence of the *p*-aminophenyl or anilino-grouping in the 2-position. The small amount of these substances available has rendered it impossible, so far, to examine their hydrolytic products in detail, but it is worth noting that in the former case the properties of the base necessitate the assumption of subsequent ring-formation involving the *p*-amino-group, whilst, in the latter, a cyclic derivative of carbamide (XXIII) is one of the possible products.



Attempts to synthesise this by the condensation of acetal or acetaldehyde with phenylcarbamide led, however, solely to *ethylenedibisphenylcarbamide* (XXIV).

EXPERIMENTAL.

Reduction of 4-Nitroglyoxaline. Formation of Glycine and Ammonia.

To 33 grams of nitroglyoxaline, dissolved in 100 c.c. of concentrated hydrochloric acid, 175 c.c. of stannous chloride solution* were gradually added, the temperature being maintained below 53° and the mixture stirred mechanically for some time after the addition was complete. The crystalline stannichloride was collected, and the filtrate concentrated, when it deposited a further quantity, the total yield being about 49 grams.

On recrystallisation from 10 per cent. hydrochloric acid, it was

* The stannous chloride solution used throughout the investigation was prepared by mixing 40 grams of stannous chloride with sufficient hydrochloric acid to form 100 c.c. of solution.

obtained in large, octahedral masses, which, after removal of tin, gave solely ammonium chloride (Found: $\text{Cl}=66.1$; $\text{NH}_3=31.6$. Calc.: $\text{Cl}=66.3$; $\text{NH}_3=31.8$; in the stannichloride, $\text{NH}_3=9.1$, 9.2 . Calc.: $\text{NH}_3=9.3$ per cent.). The residual liquor was evaporated to remove excess of acid, freed from tin, again evaporated under diminished pressure, and extracted with alcohol, which left undissolved 6.3 grams of ammonium chloride. The syrupy alcoholic extract, on solution in water and addition of picric acid, yielded only traces of an insoluble picrate, 60 grams of nitroglyoxaline giving 0.5 gram in a pure condition. This separated from water in well-defined needles, which darkened rapidly above 200° and melted at 234° (corr.), and gave analytical figures in fair agreement with *aminoglyoxaline dipicrate*, but the amount was too small to permit of its further examination (Found: $\text{C}=32.8$; $\text{H}=2.6$; $\text{N}=22.8$. $\text{C}_3\text{H}_5\text{N}_3, 2\text{C}_6\text{H}_3\text{O}_7\text{N}_3$ (541.2) requires $\text{C}=33.3$; $\text{H}=2.1$; $\text{N}=23.3$ per cent.). The residual solution was reconverted into the hydrochloride, evaporated to dryness in a vacuum, dissolved in alcohol, and submitted to fractionation. There first deposited a further 1.0 gram of ammonium chloride, then (a) 5.2 grams melting at about 174° , (b) 3.1 grams melting at about 156° , and (c) 2.8 grams melting between 130° and 140° . Further crops were obtained more readily from the mother liquor after the addition of alcoholic hydrogen chloride, and these melted between 130° and 140° . Crops (a) and (b) were united and crystallised from rather less than their own weight of water, when, on keeping, there separated 4 grams of large, flattened prisms melting at 189° (corr.), sintering some degrees earlier. This substance proved to be the sesquihydrochloride of glycine (Found: $\text{C}=25.5$; $\text{H}=6.1$; $\text{N}=14.9$; $\text{Cl}=19.1$. $(\text{C}_2\text{H}_5\text{O}_2\text{N})_2, \text{HCl}$ requires $\text{C}=25.7$; $\text{H}=5.9$; $\text{N}=15.0$; $\text{Cl}=19.0$ per cent.). The mother liquor, on further concentration, deposited a mixture of this hydrochloride and the normal hydrochloride of glycine, from which the latter was obtained on crystallisation in presence of excess of hydrochloric acid. It separated as a serrated mass of somewhat hygroscopic, flattened prisms, which melted at 182° (corr.), sintering above 150° (Found: $\text{C}=21.7$; $\text{H}=5.7$; $\text{N}=12.7$; $\text{Cl}=31.2$. $\text{C}_2\text{H}_5\text{O}_2\text{N}, \text{HCl}$ requires $\text{C}=21.5$; $\text{H}=5.4$; $\text{N}=12.6$; $\text{Cl}=31.8$ per cent.). Crop (c), and subsequent crops melting at about the same temperature, were mixed and recrystallised from alcohol, when a mass of fine, silky needles, melting at 145° (corr.) and showing no depression when mixed with a synthetic specimen of glycine ethyl ester hydrochloride, was obtained (Found: $\text{C}=34.5$; $\text{H}=7.4$; $\text{N}=10.0$; $\text{Cl}=25.0$. $\text{C}_4\text{H}_9\text{O}_2\text{N}, \text{HCl}$ requires $\text{C}=34.4$; $\text{H}=7.2$; $\text{N}=10.0$; $\text{Cl}=25.4$ per cent.).

The identity was further established by the isolation of glycine from all three hydrochlorides, the glycine melting at 247° (corr.) and showing no depression of melting point when mixed with a synthetic specimen (Found: C=31.8; H=6.9; N=18.5. $C_2H_5O_2N$ requires C=32.0; H=6.7; N=18.7 per cent.).

The ultimate alcoholic residues, which were very dark in colour, gave no further crystalline material.

Reduction of 4-Nitro-2-methylglyoxaline. Formation of Glycine, α -Amino- α -iminoethane, and Ammonia.

The reduction of 12.7 grams of nitro-2-methylglyoxaline was carried out as in the previous instance. There were first obtained 7.6 grams of ammonium stannichloride. The more soluble stannichlorides were converted into hydrochlorides in the customary manner, the solution evaporated to dryness under diminished pressure, and extracted with alcohol, leaving 3.5 grams of practically pure ammonium chloride. The alcoholic extract was concentrated to a syrup, dissolved in 50 c.c. of water, and treated with a boiling solution of 13 grams of picric acid in 250 c.c. of water, when 7.7 grams of a crude picrate were obtained. This, on recrystallisation from water, separated in glistening, orange prisms melting from 245° and melting at 252° (corr.). The yield amounted to 3.6 grams. 2.8 Grams of this picrate were converted into the hydrochloride, excess of hydrochloric acid being avoided. The resulting aqueous solution was evaporated to dryness under diminished pressure, below 50° , leaving a solid residue, which was dissolved in a little alcohol and kept. There gradually separated long, colourless, prismatic needles, which melted at 174° (corr.) and proved to be the hydrochloride of α -amino- α -iminoethane (VI. p. 669). Pinner (*Ber.*, 1884, 17, 178; "Die Iminoäther," p. 107) gives the melting point as 165° or 166 – 167° (Found: C=25.7; H=7.5; N=29.1; Cl=36.5. $C_2H_6N_2.HCl$ requires C=25.4; H=7.5; N=29.6; Cl=37.5 per cent.).

The melting point of the picrate is given by Dieckmann (*Ber.*, 1892, 25, 547) as 247° (Found: C=33.8; H=3.3; N=23.9. $C_2H_6N_2.C_6H_3O_7N_3$ requires C=33.4; H=3.2; N=24.4 per cent.).

The identity of the base was further established by the preparation of the *aurichloride*. This salt crystallises from water in fern-shaped clusters of golden-yellow needles, which melt at 266° and are anhydrous.

Found: Au=49.2.

$C_2H_6N_2.HCl.AuCl_3$ (398.1) requires Au=49.5 per cent.

The platinichloride, previously described by Pinner, separates

from water in small, orange, flattened prisms or in large, red, flattened prisms, according to the rate of crystallisation. Like the aurichloride, it is anhydrous. It melts at 242° (corr.) (Found: $\text{Pt}=37.0$. $(\text{C}_2\text{H}_6\text{N}_2)_2 \cdot 2\text{HCl} \cdot \text{PtCl}_4$ requires $\text{Pt}=37.1$ per cent.).

The residual liquor from the separation of the α -amino α -imino-ethane picrate was regenerated into the hydrochloride and evaporated to dryness, leaving a dark syrup. As this showed no tendency to crystallise, it was dissolved in absolute alcohol containing hydrogen chloride, warmed for a short time on the water-bath, and concentrated, when, on keeping, glycine ethyl ester hydrochloride gradually separated, and was identified by comparison with the synthetic product and by analysis (Found: $\text{N}=10.0$; $\text{Cl}=25.1$. $\text{C}_4\text{H}_{10}\text{O}_2\text{N} \cdot \text{HCl}$ requires $\text{N}=10.0$; $\text{Cl}=25.4$ per cent.).

The residue from the glycine ester hydrochloride yielded no further crystalline material. A small quantity of a non-nitrogenous ester was isolated, but the amount was too small to attempt its purification and identification.

Reduction of Nitro-5-methylglyoxaline. Formation of α -Alanine, 4-Amino-5-methylglyoxaline, and Ammonia.

The reduction of 11 grams of 4-nitro-5-methylglyoxaline was carried out as in the previous instances, yielding 7.5 grams of ammonium stannichloride and 1.4 grams of ammonium chloride. The syrupy, alcoholic extract was dissolved in 25 c.c. of water and treated with a boiling solution of 8 grams of picric acid in 200 c.c. of water, when there quickly separated 4 grams of fine needles contaminated with oily matter. On keeping overnight, a further 2 grams separated, mainly picric acid, and the mother liquor deposited picric acid only on concentration. The two crops were crystallised from alcohol, from which there separated clusters of long, old-gold needles, which blackened rapidly above 180° and melted and decomposed at 195° (corr.).

The picrate was converted into the hydrochloride, excess of acid being avoided. The solution, on evaporation in a vacuum at as low a temperature as possible, left a syrup, which became crystalline on mixing with a few drops of alcohol. The hydrochloride separates from alcohol in minute, colourless prisms, which melt at 189° (corr.) and are anhydrous. The crystallisation should be conducted as quickly as possible, as the alcoholic solution decomposes on keeping.

Found: $\text{C}=28.2$; $\text{H}=5.6$; $\text{N}=24.2$; $\text{Cl}=41.0$.

$\text{C}_4\text{H}_7\text{N}_3 \cdot 2\text{HCl}$ (170.0) requires $\text{C}=28.2$; $\text{H}=5.3$; $\text{N}=24.7$;
 $\text{Cl}=41.7$ per cent.

The solution of the hydrochloride reduces ammoniacal silver nitrate strongly on warming. It gives, with sodium nitroprusside on addition of sodium hydroxide, a brown colour; with sodium diazobenzene-*p*-sulphonate in sodium carbonate solution, a bright yellow colour; on treatment with nitrous acid and addition to sodium- β naphthoxide, a deep reddish-brown solution; with ferric chloride, no colour; with Fehling's solution, reduction on warming; with potassium permanganate in cold acid solution, instant reduction; with gold chloride, a brown precipitate which dissolves on warming, reduction taking place.

The properties and composition indicate that the substance is correctly formulated as 4-amino-5-methylglyoxaline (VIII, p. 669).

The *picrate* is sparingly soluble in water, but more readily so in alcohol, from which it separates in old-gold needles, which darken rapidly above 180° and melt at 195° (corr.).

Found: N = 25.3.

$C_4H_7N_3, C_6H_3O_7N_3$ (326.2) requires N = 25.8 per cent.

The *benzylidene* derivative was prepared by treating 0.23 gram of the hydrochloride in 5 c.c. of water with 0.4 gram of sodium acetate and 0.2 c.c. of benzaldehyde. On shaking vigorously, a solid product gradually formed. This was collected and washed with water and ether, in which it is sparingly soluble. It dissolves readily in alcohol, but less so in ethyl acetate, from which it separates in clusters of well-defined needles, which are anhydrous and melt and decompose at 217° (corr.), gradually darkening in colour above 190°.

Found: N = 22.9.

$C_{11}H_{11}N_3$ (185.2) requires N = 22.7 per cent.

The residual liquor from the separation of the 4-amino-5-methylglyoxaline *picrate* was reconverted into the hydrochloride and evaporated to dryness, when it left about 3 grams of a semi-solid mass, which yielded only ammonium chloride (1.0 gram) on crystallisation from water or alcohol. It was dissolved in water therefore, chlorine determined in an aliquot portion, and the hydrochloric acid in the remainder removed by the addition of the calculated quantity of freshly precipitated silver carbonate. The resulting solution was evaporated to a syrup, mixed with a little alcohol, and kept, when α -alanine gradually separated. This melted, without recrystallisation, at 237° (corr.), a synthetic specimen melting at the same temperature in the same bath, and the mixture of the two showing no depression. The identity was further confirmed by its reactions, analysis, and formation of the

copper salt (Found: C=40.1; H=8.1; N=15.4. $C_3H_7O_2N$ requires C=40.4; H=7.9; N=15.7 per cent.).

Strecker (*Annalen*, 1850, **75**, 36) found that the air-dried copper salt retained one molecule of water of crystallisation. More recently, Zelinsky and Stadnikoff (*Ber.*, 1908, **41**, 2062) failed to confirm this, and described a salt with three molecules of water of crystallisation. Both the acid obtained above and a synthetic specimen of undoubted purity yielded a copper salt with only one molecule of water of crystallisation (Found: Cu = 24.7. $(C_3H_6O_2N)_2Cu \cdot H_2O$ requires Cu=24.7 per cent.), and the salt did not gain appreciably in weight on keeping for several days in an atmosphere saturated with moisture.

Reduction of 4-p-Bromobenzenediazo-2-methylglyoxaline.

13.2 Grams of bromobenzenediazo-2-methylglyoxaline were triturated with 120 c.c. of cold hydrochloric acid and gradually treated with 72 c.c. of stannous chloride solution, the trituration being continued and the temperature maintained below 10° . The insoluble stannichloride which gradually formed was collected, and the residual liquor freed from tin and evaporated, leaving only 0.3 gram of residue, in which ammonia and *p*-bromoaniline were identified. The insoluble stannichloride was dissolved in water, freed from tin, and the resulting solution evaporated to low bulk, when, on keeping, a quantity of minute needles separated. These dissolved readily in water, but more sparingly in 10 per cent. hydrochloric acid, from which they were obtained in clusters of glistening, elongated, rhombic prisms melting at 273° (corr.).

Found: C=38.9, 39.6; H=3.9, 3.9; N=13.65.

0.2031 gave 0.2178 AgCl + AgBr, 0.2208 being required.
 $C_{10}H_{10}ON_3Br \cdot HCl$ (304.55) requires C=39.4; H=3.65; N=13.8 per cent.

The corresponding base is precipitated as a mass of minute, colourless needles on treating the concentrated aqueous solution of the hydrochloride with a molecular proportion of sodium hydroxide. It decomposes in warm aqueous solution or on exposure to the air. Dried at 60° in a vacuum, it appears to retain a molecule of water of crystallisation.

Found: C=42.1, 42.3; H=4.4, 4.5; N=14.2; Br=27.8.

$C_{10}H_{10}ON_3Br \cdot H_2O$ (286.1) requires C=41.95; H=4.2; N=14.7; Br=27.9 per cent.

The solution of the base gives no coloration with sodium diazobenzene-*p*-sulphonate in sodium carbonate solution. After treatment with nitrous acid in acid solution, a pale yellow colour

develops on addition to sodium- β -naphthoxide. An ammoniacal solution of silver nitrate is reduced in the cold. With Fehling's solution, a bluish-green precipitate is formed, which becomes dark green on warming. With sodium nitroprusside in presence of sodium hydroxide, a reddish-brown colour develops, which changes to green on acidification with acetic acid, and is discharged by excess of the reagent. The aqueous solution reduces cold aqueous acid permanganate. The base reacts with benzaldehyde, with formation of a *benzylidene* derivative, which was not obtained in a crystalline condition. The properties and composition of the base point, therefore, to its being 2-methyl-4-(2'-amino-5'-bromophenyl)-5-glyoxalone (XII, p. 670).

The *picrate* separates from water in glistening, orange plates which, when dried in the air, melt at 157° (corr.), sintering slightly above 140° . It appears to contain two molecules of water of crystallisation, one of which is lost on drying at 60° in a vacuum.

Found: in air-dried material, $N=15.65$; loss at 60° in a vacuum $=3.4$. In dried material, $N=16.2$.

$C_{10}H_{10}ON_3Br, C_6H_5O_7N_3, 2H_2O$ requires $N=15.8$. For loss of $1H_2O$, $H_2O=3.4$ per cent.

$C_{10}H_{10}ON_3Br, C_6H_5O_7N_3, H_2O$ (515.1) requires $N=16.3$ per cent.

After the separation of most of the above hydrochloride, ammonium chloride began to deposit, and a careful fractionation of the mixture revealed that the two products were present in approximately molecular proportions.

Reduction of 4-Benzeneazo-5-methylglyoxaline.

3.7 Grams were triturated with 20 c.c. of hydrochloric acid and treated, as in the previous experiment, with 12 c.c. of stannous chloride solution. The insoluble stannichlorides amounted to 6.8 grams of moist material. Tin was removed, and the resulting solution evaporated under diminished pressure to low bulk, when the hydrochloride of the base, $C_9H_{10}ON_3$ (*loc. cit.*, p. 254), separated, about 1.8 grams being obtained. The mother liquors eventually deposited ammonium chloride, and, on suitable treatment, yielded a small amount of aniline. The more soluble stannichlorides, when treated similarly, yielded a second *hydrochloride*, which separated as a matted mass of minute needles, readily soluble in water but sparingly so in alcohol. After recrystallisation from 10 per cent. hydrochloric acid, it darkened, but did not melt, at 300° . About 1.2 grams were isolated.

Found: C=46.2; H=5.4; N=15.8; Cl=26.6.

$C_{10}H_{11}ON_3 \cdot 2HCl$ (262.1) requires C=45.8; H=5.0; N=16.0;
Cl=27.0 per cent.

The solution of the hydrochloride was strongly acid to litmus. After treatment with nitrous acid, it gave a deep red coloration with sodium- β -naphthoxide. It gave no coloration with sodium diazobenzene-*p*-sulphonate in sodium carbonate solution. With sodium nitroprusside in presence of sodium hydroxide, a pale brown colour developed, which changed to green on acidification with acetic acid, and was discharged by excess of the reagent. Potassium permanganate in cold acid solution, and ammoniacal silver nitrate, were both reduced in the cold. The properties and composition of the compound indicate that it is correctly represented as 2-*p*-amino-phenyl-5-methyl-4-glyoxalone (XVIII, p. 671).

The *benzylidene* derivative was prepared by treating 0.4 gram of the hydrochloride, dissolved in 8 c.c. of water, with 0.45 gram of sodium acetate and 0.4 gram of benzaldehyde. The oily, yellow product, which became crystalline on stirring, was collected and washed with water and with ether, leaving 0.4 gram of material. This decomposed on boiling with water, and dissolved only sparingly in alcohol and ethyl acetate. It was dried at 60° in a vacuum for analysis, and then melted at 156° (corr.), softening above 153°. The figures obtained indicated that it was the *acetate* of the *mono-benzylidene* derivative.

Found: C=68.0; H=5.5; N=12.7.

$C_{17}H_{15}ON_3 \cdot C_2H_4O_2$ (337.3) requires C=67.6; H=5.7; N=12.5
per cent.

The mother liquors from the separation of the hydrochloride yielded small quantities of ammonia and aniline on suitable treatment.

Condensation of Acetaldehyde with Phenylcarbamide.

This condensation has been carried out using various conditions. For example, the phenylcarbamide was added slowly, with stirring, a large excess of freshly distilled aldehyde, or was suspended in alcohol and mixed with aldehyde or acetal in various proportions. In every case the same product was obtained—two molecules of phenylcarbamide uniting with one of the aldehyde to form *benzylidenebisphenylcarbamide*. This substance is practically insoluble in water, ether, ethyl acetate, or benzene, and very sparingly soluble in alcohol, from which it separates as a felted mass of silky needles melting at 220° (corr.).

Found: C=64.4; H=6.4; N=18.8, 18.9.

$C_{16}H_{18}O_2N_4$ (298.3) requires C=64.4; H=6.2; N=18.8 per cent.

Attempts to obtain partial hydrolysis and subsequent ring closure were unsuccessful.

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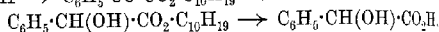
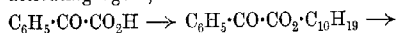
LONDON, E.C.1.

[Received, May 5th, 1920.]

LXXI.—The Behaviour of Optically Active Ester on Hydrolysis.

By ALEX. MCKENZIE and HENRY WREN.

THE first attempt made by one of us to effect an asymmetric synthesis (T., 1904, 85, 1249) involved the use of *l*-menthol as the activating agent, and was based on the following lines:

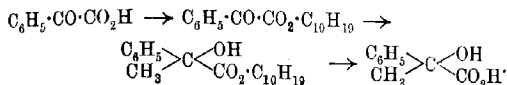


The failure to realise the synthesis desired was due in this case, as was shown later, to the racemising influence of the alcoholic alkali used in the hydrolysis of the mixture of unequal quantities of the menthyl mandelates.

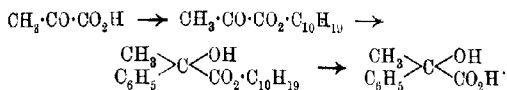
In the light of recent research (T., 1919, 115, 602), it was likely that the diastereoisomeric *l*-menthyl mandelates would be catalytically racemised during their hydrolysis, and this point was therefore now examined experimentally. The *l*-menthyl *l*-mandelate used had $[\alpha]_D -137.9^\circ$ in ethyl-alcoholic solution. Of the two active complexes in this ester, the menthyl group undergoes with alkali no optical inversion, whereas inversion does occur with the mandelic group. Accordingly, on hydrolysing the ester with an insufficiency of alcoholic alkali, and then separating the non-hydrolysed ester, the latter was no longer homogeneous, and the value for $[\alpha]_D$ had fallen to -105° . A similar examination of the isomeric *l*-menthyl *d*-mandelate gave an interesting result, inasmuch as the catalytic racemisation of this ester led to the production of a solid having a higher activity than that of the original ester; owing to the partial inversion of the *d*-mandelic group, the value for $[\alpha]_D$ in ethyl-alcoholic solution rose from -9.3° in the homogeneous ester to -51.9° in the mixture obtained by the catalytic racemisation. The observation made previously that, when either *l*-menthyl *d*-mandelate or *l*-menthyl *l*-mandelate

is hydrolysed by an excess of alcoholic alkali, the mandelic acid isolated is invariably largely racemised, is now shown to be attended by the catalytic racemisation of the esters during their hydrolysis. The *l*-bornyl mandelates have also been investigated from the same point of view (see experimental part).

The asymmetric synthesis of *l*-atrolactic acid (T., 1904, 85, 1249) was successfully accomplished in accordance with the following scheme:



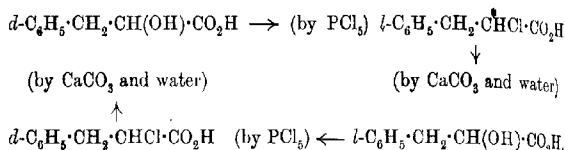
From the mixture of unequal quantities of the diastereoisomeric menthyl atrolactinates, a mixture of unequal quantities of the enantiostereoisomeric atrolactic acids with $[\alpha]_D -9.5^\circ$ in ethylalcoholic solution was obtained after the complete elimination of the menthol. The *d*-acid was also asymmetrically synthesised (T., 1906, 89, 365), using pyruvic acid as the starting point:



Subsequent research has suggested that the success of those syntheses was due to the stability of the atrolactic complex during the hydrolysis of the menthyl esters, since the labile hydrogen atom in mandelic acid is absent in atrolactic acid, the stable methyl group being present instead, with the result that isomotropic change does not occur (T., 1915, 107, 702). The direct proof, however, that this is the correct interpretation was lacking, and it is now submitted in the present paper. *l*-Menthyl atrolactinate was accordingly prepared, and found to melt at $55.5-56^\circ$ and to have $[\alpha]_D^{25} -102.7^\circ$ in chloroform solution. After hydrolysis by an excess of alcoholic alkali, it gave practically pure atrolactic acid. Again, when the ester was hydrolysed with half the quantity of alcoholic alkali requisite for complete hydrolysis, the non-hydrolysed ester gave a value for $[\alpha]_D$, which was not far short of that for the pure ester. Further, the fractional hydrolysis of *l*-menthyl *dl*-atrolactinate was examined in the expectation that the confusing results which have been obtained in other cases with esters containing mobile hydrogen atoms would not be encountered in this case. This expectation was realised. On partial hydrolysis, a levorotatory acid was obtained from the alkali salts, an indication that *l*-menthyl *l*-atrolactinate is hydrolysed

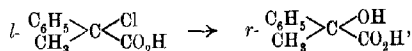
more quickly than is *l*-menthyl *d*-atrolactinate. The non-hydrolysed ester should, therefore, contain an excess of the *d*-atrolactinate, which, on hydrolysis, should give a dextrorotatory acid, and this was borne out by experiment.

An examination of the hydrolysis of esters of the optically active α -hydroxy- β -phenylpropionic acids was also included in the scope of the present investigation. We had previously shown (T., 1910, 97, 1355) that those acids can be interconverted, thus:

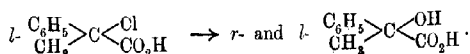


The ease with which the pure hydroxy-acid could be prepared from its enantiostereoisomeride was very striking in this case, and it was apparent that the racemisation phenomena which accompanied on so many occasions the Walden inversions investigated by one of us and his co-workers were much less pronounced than usual. It is, indeed, somewhat remarkable that in the study of the Walden inversion, racemisation occurs so frequently when the displacement is effected with compounds containing a phenyl group in direct attachment to the asymmetric carbon atom. Now, α -hydroxy- β -phenylpropionic acid has the phenyl group separated from the asymmetric atom by a methylene group, and to this circumstance may be ascribed the behaviour of this acid, to which reference has just been made.

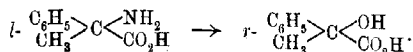
The type of racemisation with which one has to deal in connexion with reactions involving displacement of groups, whether accompanied with configurational change or not, is obviously different from the type when an optically active ester is hydrolysed with an excess of alcoholic alkali. An illustration of this difference is afforded with compounds containing a tertiary asymmetric atom (T., 1910, 97, 1016). Complete racemisation occurs when the chlorine in *l*- α -chloro- α -phenylpropionic acid is removed by the action of water,



whilst a partly racemised atrolactinic acid is formed by the action of water and silver oxide,



Similarly, by the action of nitrous acid on *l*-α-amino-α-phenylpropionic acid (T., 1912, 101, 390), the resulting atrolactic acid is quite inactive,



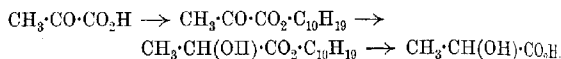
On the one hand, these examples show clearly that the absence of a mobile hydrogen atom in the α-position with respect to the carboxyl group does not prevent racemisation coming into play during the interchange of groups provided that one of the groups attached to the asymmetric atom is the phenyl group. On the other hand, when the behaviour of an ester, such as *l*-menthyl atrolactinate, towards alcoholic alkali is considered, it is now proved that the active atrolactic acid can be recovered practically unracemised.

The study of the hydrolysis of esters of optically active α-hydroxy-β-phenylpropionic acid was accordingly made. Ethyl *l*-α-hydroxy-β-phenylpropionate, $\text{C}_6\text{H}_5\cdot\text{CH}_2\cdot\text{CH}(\text{OH})\cdot\text{CO}_2\text{Et}$, for instance, has a hydrogen atom associated with a hydroxyl group in the α-position relatively to the carbethoxy-group, and in this respect it resembles ethyl *l*-mandelate, the behaviour of which on hydrolysis has been carefully investigated. On the other hand, it differs from ethyl *l*-mandelate in not having its phenyl group attached to the asymmetric atom.

The action of an excess of alkali on *d*-α-hydroxy-β-phenylpropionic acid was accordingly examined, when it was found that the recovered acid was non-racemised (table I), a behaviour different from that of *l*-mandelic acid (T., 1919, 115, 602). Ethyl *l*-α-hydroxy-β-phenylpropionate was then hydrolysed with an excess of alkali, the results being recorded in table II, from which it will be seen that in each experiment the recovered acid was practically optically pure. Moreover, there was practically no catalytic racemisation on the partial hydrolysis of the same ester with alcoholic alkali, the non-hydrolysed ester having $[\alpha]_D -28.0^\circ$ in carbon disulphide solution, whereas the value for the pure ester is $[\alpha]_D -28.8^\circ$. *l*-Menthyl *d*-α-hydroxy-β-phenylpropionate was also prepared and examined from the same point of view, in order to contrast it with *l*-menthyl *d*-mandelate.

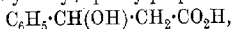
The difference between the behaviour of the esters of *l*-mandelic acid and *l*-α-hydroxy-β-phenylpropionic acid on hydrolysis is accordingly pronounced. So far as racemisation comes into play in the hydrolysis of an optically active ester by alcoholic alkali, it is now clear that, although compounds of the type $\text{R}\cdot\text{CH}(\text{OH})\cdot\text{CO}_2\text{R}'$ present a system prone to racemisation in virtue of the mobile

hydrogen atom being in the α -position, this circumstance is not in itself a factor in promoting racemisation unless R is an aromatic residue in direct attachment to the asymmetric atom. In the event of R being an aliphatic group, it may be argued that this system would probably be stable, so far as racemisation by alkali is concerned, and there is a certain amount of experimental evidence in favour of this. For example, although it had not been found possible to effect the asymmetric synthesis of mandelic acid on the lines outlined at the start of this paper, a positive result was reached when the phenyl group was displaced by a methyl one, inasmuch as the asymmetric synthesis of *l*-lactic acid could be accomplished by the agency of *l*-menthol (T., 1905, **87**, 1373), using pyruvic acid as the starting point,

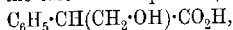


A similar result was obtained by the use of *l*-borneol (T., 1906, **89**, 688), whilst *d*-lactic acid was asymmetrically synthesised by means of *d*-amyl alcohol (T., 1909, **95**, 544). The influence of the phenyl group as compared with the methyl group is thus shown clearly, inasmuch as the diastereoisomeric *l*-menthyl lactates are much more stable towards the racemising influence of alcoholic alkali than are the diastereoisomeric *l*-menthyl mandelates, since from a mixture of *l*-menthyl *d*-lactate and *l*-menthyl *l*-lactate containing a preponderance of one of them, it was possible to obtain an optically active lactic acid when the ester mixture was completely hydrolysed.

β -Hydroxy- β -phenylpropionic acid and tropic acid are isomeric with atrolactic acid and α -hydroxy- β -phenylpropionic acid. The methyl ester of *d*- β -hydroxy- β -phenylpropionic acid,

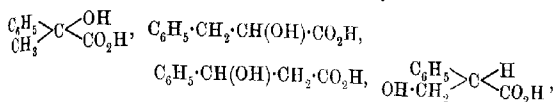


gives the optically pure *d*-acid on hydrolysis with alcoholic potassium hydroxide (T., 1913, **103**, 112), and it will be noted that the hydrogen atom associated with the hydroxy-group is in this case in the β -position, a system which should be stable so far as racemisation of its esters on hydrolysis is concerned, even although a phenyl group is attached to the asymmetric atom. On the other hand, the reverse is the case with tropic acid,



where we have a system which might be expected to behave like mandelic acid; Gadamer's experiments on the racemisation of ethyl *d*-tropate on hydrolysis (*J. pr. Chem.*, 1913, [ii], **87**, 312) bear this out.

The behaviour on hydrolysis of the optically active esters of the various isomeric "phenyl-lactic" acids, namely,



has thus been examined fairly completely.

EXPERIMENTAL.

Catalytic Racemisation of the Diastereoisomeric l-Menthyl Mandelates.

The *l*-menthyl *l*-mandelate used had $[\alpha]_D -137.9^\circ$ in ethyl-alcoholic solution. Ten c.c. of the solution of sodium in ethyl alcohol employed for its partial hydrolysis required 14.3 c.c. of 0.101*N*-sulphuric acid for neutralisation, and of this solution, 83 c.c. were added to a solution of the ester (7.2 grams) in 100 c.c. of ethyl alcohol. After twenty-two hours at the ordinary temperature, 130 c.c. of ethyl alcohol were removed from the neutral liquid by distillation, and 1.1 grams of sodium salt separated on cooling. The acid obtained from this was a mixture of *r*- and *l*-mandelic acids with $[\alpha]_D -53^\circ$ in ethyl-alcoholic solution, the pure *l*-acid having $[\alpha]_D$ about -152° in the same solvent. After the removal of the sodium salt, the filtrate was evaporated, and the menthol separated from the residue by distillation in a current of steam. The residual solid ester (2.7 grams) gave $[\alpha]_D -105^\circ$ ($c=1.6$) in ethyl-alcoholic solution. The solution of sodium salt from which the ester had been separated was then acidified, and the resulting mandelic acid gave $[\alpha]_D -81.9^\circ$ in ethyl-alcoholic solution.

An examination of the isomeric *l*-menthyl *d*-mandelate with $[\alpha]_D -9.3^\circ$ in ethyl-alcoholic solution was next made. Six grams were dissolved in 96 c.c. of ethyl-alcoholic potassium hydroxide (0.1077*N*), the amount calculated for complete hydrolysis being 192.1 c.c. Thereafter, the liquid was kept for two days at the ordinary temperature, the ethyl alcohol was removed from the neutral solution, and water was then added. The mixture of the non-hydrolysed ester and the menthol was then extracted with ether, whilst the mandelic acid was obtained from the aqueous residue in the customary manner. The fact that the recovered acid had $[\alpha]_D +91.2^\circ$ in aqueous solution indicated the presence in it of a considerable quantity of the racemic acid. From the ethereal extract containing the non-hydrolysed ester and menthol, the ether was removed, and the oil distilled in a current of steam

to separate the menthol. The recovered solid ester, which was quite free from uncombined menthol, gave $[\alpha]_D -51.9^\circ$ ($c=4.171$) in ethyl-alcoholic solution.

Catalytic Racemisation of the Diastereoisomeric l-Bornyl Mandelates.

The *l*-bornyl *l*-mandelate used had $[\alpha]_D -86.0^\circ$ in ethyl-alcoholic solution (T., 1907, **91**, 789). Nineteen c.c. of an ethyl-alcoholic solution of potassium hydroxide (0.6532*N*) were added to a solution of 7.05 grams of the ester in 100 c.c. of ethyl alcohol. The solution was treated as already described for the menthyl *d*-mandelate. The recovered mandelic acid had $[\alpha]_D -106.2^\circ$ in aqueous solution, whereas the optically pure acid has a value about 50° higher than this. As was expected, the rotation of the recovered ester was less laevorotatory than that of the homogeneous ester, the value obtained being $[\alpha]_D -58.0^\circ$ in ethyl-alcoholic solution.

When a similar experiment was carried out with *l*-bornyl *d*-mandelate, the non-hydrolysed ester had a dextrorotation less than that of the original ester, which had $[\alpha]_D +23.0^\circ$ in ethyl-alcoholic solution. The ester (10.3 grams) was dissolved in 146 c.c. of ethyl alcohol, and 28 c.c. of ethyl-alcoholic potassium hydroxide (0.6532*N*) were added. The recovered mandelic acid had $[\alpha]_D +105.5^\circ$ in aqueous solution, whereas the non-hydrolysed ester had $[\alpha]_D +15.3^\circ$ in ethyl-alcoholic solution.

We are indebted to Miss Isobel Agnes Smith for carrying out these experiments with the bornyl mandelates.

Hydrolysis of l-Menthyl l-Atrolactinate.

l-Atrolactic acid (T., 1910, **97**, 1016) was esterified by heating on a boiling-water bath for fifteen hours with *l*-menthol and a small quantity of concentrated sulphuric acid. The crude solid ester was finally crystallised from light petroleum at the temperature of a freezing mixture of ice and salt.

l-Menthyl *l*-atrolactinate, $\text{Me} \begin{array}{c} \text{Ph} \\ \diagup \\ \text{C} \\ \diagdown \\ \text{CO}_2\text{C}_{10}\text{H}_{19} \end{array} \begin{array}{c} \text{OH} \\ \diagup \\ \text{C} \\ \diagdown \end{array}$, separates from light petroleum in colourless, silky needles, and melts at $55.5-56^\circ$. It is readily soluble in this solvent at the ordinary temperature, and it is also readily soluble in the common organic solvents:

0.1200 gave 0.3300 CO_2 and 0.0997 H_2O . $\text{C}=75.0$; $\text{H}=9.3$.

$\text{C}_{19}\text{H}_{28}\text{O}_3$ requires $\text{C}=74.9$; $\text{H}=9.3$ per cent.

Its specific rotation was determined in the following solvents:

(a) Acetone:

$$l=2, c=1.982, \alpha_D^{25} = -2.96^\circ, [\alpha]_D^{25} = -74.7^\circ.$$

(b) Ethyl alcohol:

$$l=2, c=1.2741, \alpha_D^{20} = -2.30^\circ, [\alpha]_D^{20} = -90.3^\circ.$$

(c) Chloroform:

$$l=2, c=1.4215, \alpha_D^{14} = -2.92^\circ, [\alpha]_D^{14} = -102.7^\circ.$$

Complete Hydrolysis with Alcoholic Alkali.—The ester (1.6 grams) was dissolved in 40 c.c. of ethyl-alcoholic potassium hydroxide (0.202*N*), the amount calculated for complete hydrolysis being 26 c.c. After four days at the ordinary temperature, the acid was isolated, and its rotation when determined in ethyl-alcoholic solution showed that no racemisation had occurred during the hydrolysis. The value was $[\alpha]_D = -37.2^\circ$ ($c=1.398$). The optically pure acid has $[\alpha]_D = -37.7^\circ$.

Partial Hydrolysis with Alcoholic Alkali.—The ester (1.9 grams) was dissolved in 16 c.c. of ethyl-alcoholic potassium hydroxide (0.193*N*), the quantity calculated for complete hydrolysis being 32.4 c.c. After twenty-four hours at the ordinary temperature, the treatment was similar to that adopted in the experiment with *l*-menthyl *d*-mandelate. The residual ester was not appreciably hydrolysed during the prolonged distillation in a current of steam when the menthol was being removed.

The recovered ester gave $[\alpha]_D = -99.8^\circ$ ($c=1.988$) in chloroform solution.

The recovered acid melted at $114.5\text{--}116^\circ$ (the pure *l*-acid melts at $116\text{--}117^\circ$); its rotation in ethyl-alcoholic solution gave $[\alpha]_D = -36.1^\circ$ ($c=1.733$).

The optical activity is impaired during the distillation of *l*-menthyl *l*-atrolactinate under diminished pressure. After being distilled twice (b. p. $187.5\text{--}188.5^\circ/11$ mm.), it readily solidified, and then melted indefinitely at $41\text{--}51^\circ$, whilst its rotation in chloroform solution gave a low value, namely, $[\alpha]_D = -91.6^\circ$. This product was accordingly hydrolysed with an excess of ethyl-alcoholic potassium hydroxide, and the acid, which was isolated in the usual manner, had $[\alpha]_D = -31.0^\circ$. It appeared probable that the ester had undergone partial racemisation under the influence of heat.

Fractional Hydrolysis of l-Menthyl dl-Atrolactinate.

l-Menthyl *dl*-atrolactinate, prepared by the esterification of anhydrous *r*-atrolactic acid by heating with menthol and a small

quantity of concentrated sulphuric acid on a boiling-water bath for twenty-five hours, is a colourless oil which boils at 194–194.5°/11 mm.:

0.1329 gave 0.3663 CO₂ and 0.1119 H₂O. C=75.2; H=9.4.

C₁₉H₂₈O₃ requires C=74.9; H=9.3 per cent.

The following determinations of its specific rotation were made:

(a) Carbon disulphide:

$$l=2, c=2.408, \alpha_D^{20} - 2.69^\circ, [\alpha]_D^{20} - 55.9^\circ.$$

(b) Benzene:

$$l=2, c=2.1225, \alpha_D^{15} - 2.71^\circ, [\alpha]_D^{15} - 63.8^\circ.$$

(c) Acetone:

$$l=2, c=2.039, \alpha_D^{14} - 2.70^\circ, [\alpha]_D^{14} - 66.2^\circ.$$

(d) Chloroform:

$$l=2, c=2.014, \alpha_D^{11} - 2.80^\circ, [\alpha]_D^{11} - 69.5^\circ.$$

(e) Ethyl alcohol:

$$l=2, c=2.3955, \alpha_D^{15} - 3.45^\circ, [\alpha]_D^{15} - 72.0^\circ.$$

A solution of the ester (2 grams) in 20 c.c. of ethyl-alcoholic potassium hydroxide (0.93*N*) was boiled for one hour, the amount of alkali requisite for the complete hydrolysis being 7.1 c.c. The acid isolated was optically inactive.

The fractional hydrolysis was conducted with 4 grams of the ester to which 7.1 c.c. of ethyl-alcoholic potassium hydroxide (0.93*N*) were added, this being half of the amount necessary for complete hydrolysis. Boiling of the solution was maintained for two hours. The acid obtained from the potassium salt after separation from menthol and menthyl esters amounted to 0.8759 gram, and it had $[\alpha]_D - 1.7^\circ$ in ethyl-alcoholic solution. The hydrolysis of the residual menthyl esters was then completed with 15 c.c. of ethyl-alcoholic alkali (0.93*N*). The resulting acid (0.8394 gram) was dextrorotatory, having $[\alpha]_D + 2.3^\circ$ in ethyl-alcoholic solution.

Action of Potassium Hydroxide on d- α -Hydroxy- β -phenylpropionic Acid.

d- α -Hydroxy- β -phenylpropionic acid (T., 1910, **97**, 1355) was treated under various conditions with an excess of potassium hydroxide dissolved in water or in ethyl alcohol. The solution was then neutralised, water added, and the ethyl alcohol expelled. The recovered acid was examined polarimetrically in ethyl-alcoholic solution. The pure *d*-acid has $[\alpha]_D + 18.5^\circ$ (*loc. cit.*).

TABLE I.

0.83 Gram of acid was taken in each experiment. In order to neutralise this, 5.4 c.c. of alkali (0.93*N*) are required.

Alkali (0.93 <i>N</i>).	Conditions.	$[\alpha]_D$ of recovered acid.
60 c.c. aqueous.	15 days at ord. temp.	+18.3° ($c = 3.24$)
"	20 hours at 70°.	18.3° ($c = 3.44$)
60 c.c. alcoholic.	15 days at ord. temp.	18.0° ($c = 3.14$)
"	20 hours at 70°.	18.2° ($c = 3.49$)

Hydrolysis of Ethyl 1- α -Hydroxy- β -phenylpropionate.

The *l*-acid was converted into its ethyl ester, which, after crystallisation from light petroleum (b. p. 60–80°), gave the value $[\alpha]_D^{25} -23.1^\circ$ in benzene solution, whereas the value previously quoted is $[\alpha]_D -22.6^\circ$ (T., 1911, 99, 1922). A somewhat higher value is obtained when carbon disulphide is used as the solvent:

$$l=2, c=2.306, \alpha_D^{25} -1.33^\circ, [\alpha]_D^{25} -28.8^\circ.$$

Complete Hydrolysis.—The results obtained by hydrolysing the ester with a slight excess of aqueous or alcoholic alkali are expressed in the following table.

TABLE II.

Ester. Grams.	Alkali.	Alkali required. c.c.	Conditions.	$[\alpha]_D$ of recovered acid.
1.0247	6.2 c.c. aqueous (0.93 <i>N</i>).	5.7	3 hours at 70°.	-17.9° ($c = 4.04$)
0.8696	10 c.c. alcoholic (0.93 <i>N</i>).	4.8	1 day at ord. temp.	18.0° ($c = 2.67$)
0.8696	10 c.c. alcoholic (0.93 <i>N</i>).	4.8	2½ hours at 70°.	17.9° ($c = 2.28$)
0.9957	47 c.c. alcoholic (0.1105 <i>N</i>).	46.4	3 hours at 70°	17.9° ($c = 3.85$)

Partial Hydrolysis with Alcoholic Alkali.—The ester (4 grams) was dissolved in 94 c.c. of ethyl-alcoholic potassium hydroxide (0.1105*N*), the quantity required for complete hydrolysis being 187 c.c.

The solution was divided into two equal parts: (a) Kept at the ordinary temperature for twenty-four hours, at the end of which time the solution was neutral. The alcohol was removed by evaporation, water added, and the non-hydrolysed ester extracted with ether. The aqueous solution was then acidified, and the hydroxy-acid extracted with ether. The recovered ester gave the value $[\alpha]_D -28.0^\circ$ for $c=3.889$ in carbon disulphide solution, whilst

C O*

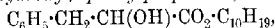
the recovered acid gave $[\alpha]_D -17.8^\circ$ for $c=3.262$ in ethyl-alcoholic solution.

(b) Heated at 70° for five hours. The recovered ester had $[\alpha]_D -28.3^\circ$ for $c=2.226$ in carbon disulphide solution, whilst the recovered acid had $[\alpha]_D -18.2^\circ$ for $c=3.777$ in ethyl-alcoholic solution.

Hydrolysis of l-Menthyl d- α -Hydroxy- β -phenylpropionate.

d- α -Hydroxy- β -phenylpropionic acid was esterified by heating with *l*-menthol for seven hours at $120-130^\circ$ in an intermittent current of hydrogen chloride. The resulting ester was separated from acid and menthol, and purified by crystallisation from light petroleum (b. p. $40-60^\circ$).

l-Menthyl d- α -hydroxy- β -phenylpropionate,



separates from light petroleum (with which it readily forms super-saturated solutions) in matted aggregates of silky needles; it is readily soluble in the hot and sparingly so in the cold solvent. It is also readily soluble in the common organic solvents. It melts at $63-63.5^\circ$:

0.1114 gave 0.3070 CO_2 and 0.0923 H_2O . $C=75.2$; $H=9.3$.

$C_{19}H_{25}O_3$ requires $C=74.9$; $H=9.3$ per cent.

The specific rotation was determined in various solvents:

(a) Benzene:

$$l=2, c=1.4005, \alpha_D^{17} -0.76^\circ, [\alpha]_D^{17} -27.1^\circ.$$

(b) Chloroform:

$$l=2, c=2.697, \alpha_D^{15.5} -1.99^\circ, [\alpha]_D^{15.5} -36.9^\circ.$$

(c) Acetone:

$$l=2, c=0.871, \alpha_D -0.86^\circ, [\alpha]_D -49.4^\circ.$$

The ester (1.1 grams) was dissolved in 40 c.c. of ethyl-alcoholic potassium hydroxide (0.1105*N*), the amount calculated for complete hydrolysis being 33 c.c. After eight hours at 70° , the acid was isolated. It melted at $121-123.5^\circ$, whereas the pure *d*-acid melts at $124-125^\circ$. That very slight racemisation had occurred during the hydrolysis is indicated by the somewhat low value for the specific rotation in ethyl-alcoholic solution, namely, $[\alpha]_D +17.4^\circ$ ($c=2.586$).

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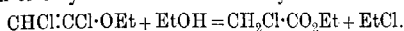
[Received, May 1st, 1920.]

MUNICIPAL TECHNICAL INSTITUTE,
BELFAST.

LXXII.—*The Use of $\alpha\beta$ -Dichlorovinyl Ethyl Ether for the Production of Chloroacetates and Acid Chlorides.*

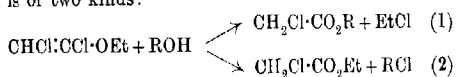
By HOLLAND CROMPTON and PAULE LAURE VANDERSTICHELE.

THE production of ethyl chloroacetate, and eventually of chloroacetic acid, by the action of water on $\alpha\beta$ -dichlorovinyl ethyl ether has been the subject of a large number of patents. By using dry hydrogen chloride in place of water, chloroacetyl chloride is obtained (D.R.-P. 222194), and Imbert found (D.R.-P. 212592) that dichlorovinyl ethyl ether and ethyl alcohol react, with the production of ethyl chloroacetate and ethyl chloride:

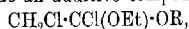


He also states that methyl chloroacetate is formed if methyl alcohol is used in place of ethyl alcohol.

We find that $\alpha\beta$ -dichlorovinyl ethyl ether enters into a large number of reactions of the above type. It is attacked, and usually with great readiness, when heated with alcohols, phenols, or acids. Action is of two kinds:



and it seems likely that an additive compound,



is first formed, which decomposes into the products (1) and (2). Our experience is that alcohols give the products of both reactions, but that (1) predominates, except in the case of methyl alcohol. Phenols give the products of (1) only, and usually in excellent yield. Acids react mainly in accordance with (2), the products being ethyl chloroacetate and an acid chloride. The yields are variable, but it would appear that reactions of the above type could be used in certain cases for the production of chloroacetates or acid chlorides.

To prepare $\alpha\beta$ -dichlorovinyl ethyl ether, sodium is dissolved in dry alcohol in sufficient quantity to form a saturated solution of sodium ethoxide. Trichloroethylene is then added in the proportion of one molecule of trichloroethylene to one and a-half atoms of sodium. Heat is applied until action commences, when further heating is unnecessary. The product, when cold, is mixed with a large volume of distilled water, and the oil which separates is washed, dried with calcium chloride, and rectified. The main

portion distils at 122—126°, and this is nearly pure dichlorovinyl ethyl ether. The yield is about 70 per cent. of the theoretical.

For the action on alcohols or phenols, the substance was employed in as dry a state as possible and mixed with the ether in equivalent quantity. Heat was applied to start the reaction, but further heating was often unnecessary, except towards the end of the process. In other cases, however, heat had to be applied throughout to maintain the reaction. The products were separated by fractional distillation, or, where possible, by crystallisation. The chloroacetate of the alcohol or phenol radicle was finally identified by analysis. Ethyl chloroacetate was recognised by heating the appropriate fraction with aniline, thus forming the characteristic ester of phenylglycine.

The results with methyl alcohol were not in accordance with Imbert's statement. Ethyl chloroacetate was the main product and methyl chloroacetate was only produced in relatively small quantity. Ethyl alcohol gave the expected excellent yield of ethyl chloroacetate. *iso*Amyl, heptyl, allyl, and menthyl alcohols were each found to yield the chloroacetate of the alcohol radicle, but ethyl chloroacetate was also formed in these cases. With glycerol and mannitol, no uniform product could be obtained.

All the phenols examined gave good yields of the aryl chloroacetate, but in no case was ethyl chloroacetate detected. The compounds dealt with were phenol, *o*-cresol, guaiacol, α - and β -naphthol, resorcinol, and quinol. The two latter compounds gave the bischloroacetates. *β -Naphthyl chloroacetate*, $C_{12}H_9O_2Cl$, which has not been previously described, crystallises in small colourless leaflets melting at 95°. It dissolves readily in hot alcohol, and is much less soluble in the cold.

The monobasic acids, the behaviour of which with dichlorovinyl ethyl ether was examined, were acetic, chloroacetic, phenylacetic, benzoic, anisic, and α -naphthoic. In most cases action occurred readily on heating, but it was necessary to apply heat continuously throughout the process. Some hydrogen chloride was evolved in each case, but ethyl chloride was only observed in the case of anisic acid and of naphthoic acid. Ethyl chloroacetate was always present as the chief product of the reaction. The acid chloride formed at the same time was isolated in a pure state in the reactions with acetic, chloroacetic, and benzoic acids. In the other cases, the acid chloride was not obtained pure, but its presence was indicated by the immediate production of the corresponding amide on treating the appropriate fraction with ammonia.

Two dicarboxylic acids, oxalic and succinic, were also dealt with. Ethyl chloroacetate was formed in quantity in each case, but the

acid chloride was not obtained, succinic acid being almost entirely converted into succinic anhydride. This may be explained by the reaction taking place in stages, the monochloride of the acid being first formed. The monochloride of oxalic acid, as Staudinger has pointed out (*Ber.*, 1908, **41**, 3558), is extraordinarily unstable and decomposes at once into hydrogen chloride, carbon monoxide, and carbon dioxide. The monochloride of succinic acid would naturally pass into succinic anhydride.

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[Received, March 9th, 1920.]

LXXIII.—*Electrolysis of Hydrogen Bromide in Liquid Sulphur Dioxide.*

By LANCELOT SALISBURY BAGSTER and GEORGE COOLING.

THE work to be described in this paper was suggested by some results previously published by Bagster and Steele (*Trans. Faraday Soc.*, 1912, **8**, 51), who found that, although dry solutions of hydrogen bromide in liquid sulphur dioxide were practically non-conducting, the addition of water, which itself in solution is also non-conducting, allowed current to flow freely, hydrogen being discharged at the cathode and bromine at the anode, whilst water was carried from anode to cathode and deposited there. The conclusion drawn was that combination between the two solutes preceded conduction, and comparison with the similar behaviour of organic compounds led to the suggestion that the water and hydrogen bromide united to form an oxonium compound which was electrolytic in character.

The present work was undertaken in order to examine the nature of this phenomenon carefully, and in particular to obtain quantitative information regarding the products formed during electrolysis and regarding the compound from which the products are derived. As an alternative explanation to that already offered, it may be suggested that a simple hydrate type of compound is formed analogous to $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$, and that the deposition of water at the cathode is brought about during electrolysis by the loss of the hydrogen bromide holding it in solution. The experimental evidence, however, renders this suggestion untenable.

The experiments to be described were carried out at the temperature of boiling liquid ammonia, which was used as

refrigerant. The solutions were prepared and the experiments carried out in large test-tubes immersed in the ammonia contained in Dewar flasks. The tubes were closed by rubber stoppers carrying the electrodes and tubes for introducing the gaseous sulphur dioxide, which condensed to liquid at the temperature of the ammonia. Water was placed in the tube before placing the latter in the ammonia. The water remained as a solid at the bottom of the test-tube after the introduction of the sulphur dioxide, but on passing gaseous hydrogen bromide into the liquid, two layers were formed, the lower one consisting of a solution of sulphur dioxide and hydrogen bromide in water, and the upper one of a solution of water and hydrogen bromide in sulphur dioxide.

In the course of preliminary experiments, it was found that if the upper layer were syphoned off and used for the electrolysis, the current soon fell in value, whilst no water was deposited at the cathode, sulphur being liberated there in quantity. When the lower layer was allowed to remain in the vessel during the electrolysis, the current maintained its initial value, whilst water appeared at the cathode, very little sulphur being deposited. The water deposited at the cathode collected as small drops, which fell to the bottom of the apparatus.

The probable explanation of the need for the presence of the second layer is that it serves to maintain a saturated solution, and that otherwise the solution near the electrodes becomes depleted of water and hydrogen bromide, a different type of reaction then setting in. In the electrolysis experiments to be described, the second layer was present, but the electrodes were so arranged that conduction and electrolysis took place in the upper solution with the sulphur dioxide as solvent.

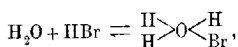
Two series of quantitative investigations were carried out, namely, (1) solubility determinations, and (2) determination of the quantity of water deposited at the cathode. In both cases the following method of analysis was adopted for the mixtures and solutions obtained, which contained water, sulphur dioxide, and hydrogen bromide. The sample was introduced into a weighed vessel, and most of the sulphur dioxide and some of the hydrogen bromide boiled off at a temperature below 0° , the gases being absorbed in sodium hydroxide solution. The bromide and sulphite in the hydroxide solution were determined by standard methods. Trial showed that the water was not appreciably distilled and could be estimated in the residue. For this purpose, a weighed quantity of concentrated sodium hydroxide solution was added to the already weighed vessel containing the water and residual sulphur dioxide and hydrogen bromide, the vessel then being "

weighed. A determination of the bromide and sulphite in the solution enabled the water to be calculated by difference. Tests with known quantities of the constituents showed that the method was accurate to about 1 per cent.

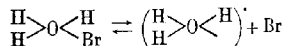
For the solubility determinations, the solutions were prepared by adding excess of water to the sulphur dioxide and passing into the liquid varying amounts of hydrogen bromide. The solutions were well shaken and allowed to settle, the clear, upper layer being syphoned off for analysis. The results of the analyses are given in the following table:

Hydrogen bromide. Gram.	Water. Gram.	Gram-mol. of hydrogen bromide.	Gram-mol. of water.	Dissolved in 2 grams of sulphur dioxide.
0.568	0.126	0.0070	0.0070	10.2
0.970	0.214	0.0120	0.0119	15.6
0.435	0.096	0.0054	0.0053	11.0
0.650	0.145	0.0080	0.0080	9.7

It will be seen that the water and hydrogen bromide are found in the solutions in equimolecular proportion, and as water itself is but sparingly soluble in sulphur dioxide, it may be concluded that a compound, $\text{H}_2\text{O} \cdot \text{HBr}$, is formed. Whether this compound is an oxonium derivative or a simple hydrate can be decided from observation during electrolysis. If the deposit of water at the cathode were formed by precipitation of dissolved water as the hydrogen bromide holding it in solution was destroyed by electrolysis, a similar deposit should appear at the anode. In no case was the slightest indication of such deposit observed, and it may be concluded that a true oxonium compound is formed:



and as the hydrogen and water liberated during electrolysis both appear at the cathode, this compound must ionise as follows:



the H_3O^+ ion losing its charge at the electrode during electrolysis and forming hydrogen and water.

This formula and mechanism of reaction have been previously suggested by Bagster and Steele, but no quantitative evidence was available, and the formula adopted was based on speculation. It was also shown in the paper referred to that Faraday's law holds for solutions in sulphur dioxide, and it is to be expected that the water and hydrogen liberated will correspond with the quantity of silver deposited in a silver voltameter. It was shown, however,

that in the case of the hydrogen this expectation was not realised, and further careful experiments lately carried out gave no better result. As the solutions were always coloured yellow, probably by traces of bromine, it is probable that the hydrogen was destroyed by reaction at the electrode. The water deposited, however, has been estimated, and found to correspond closely with the quantity predicted by the theory put forward. For this determination, the cathode consisted of a platinum wire sealed through the bottom of a glass tube, the deposited water being collected in a small glass cup suspended underneath. At the end of the experiment, the cup was transferred to the weighed vessel and its contents analysed, as already described.

Two experiments were carried out, with the following results:

Silver in voltameter. Gram.	Water deposited. Gram.	Milligram equivalent of silver.	Milligram equivalent of water.
0.120	0.022	1.11	1.22
0.224	0.037	2.08	2.06

It will be seen from the results that one equivalent of water is liberated at the cathode in the sulphur dioxide solution for every equivalent of silver deposited in the voltameter. This is the result to be expected if the explanation offered as to the mechanism of reaction is correct.

This work has seemed of sufficient importance to publish, as it is probable that similar compounds exist in aqueous solutions of halogen hydrides, quite apart from hydrates of the ordinary type and that they may take part in the electrolysis and reactions of such solutions.

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[Received, May 1st, 1920.]

LXXIV.—*Some Properties of Benzanthrone.*

By ARTHUR GEORGE PERKIN.

DURING some experiments with benzanthrone, attention was arrested by the deep blood-red coloration which it yields when dissolved in concentrated sulphuric acid. As the addition of water to this solution reprecipitates quantitatively unchanged benzanthrone, there thus seemed evidence of the formation of an oxonium salt. On diluting the acid solution with acetic acid, or by adding sulphuric acid to benzanthrone dissolved in acetic acid

however, no insoluble compound of this nature could be isolated. In attempting again to prepare a ferrichloride by the addition of anhydrous ferric chloride to an acetic acid solution of benzanthrone, diluted with a few drops of hydrochloric acid, only the unchanged substance separated on cooling, but on reducing the amount of hydrochloric acid to a minute proportion, red needles were at first deposited, although these gradually became yellow owing to re-conversion into benzanthrone. Ultimately, it was ascertained that, by avoiding the addition of hydrochloric acid, the desired compound could be readily prepared. To a solution of 0.5 gram of benzanthrone in 20 c.c. of glacial acetic acid, 0.5 gram of anhydrous ferric chloride in the minimum of boiling acetic acid was added. The deep brown liquid, on partial cooling, became semi-solid, owing to the separation of red needles of the *ferrichloride*, and these were collected, washed with acetic acid, and dried at 100°. As the product on treatment with water was readily converted into benzanthrone, this reaction was employed for analytical purposes.

Found: $C_{17}H_{10}O = 69.5$, 69.8 ; $Fe = 8.80$; $Cl = 21.7$.

$(C_{17}H_{10}O)_2HFeCl_4$ requires $C_{17}H_{10}O = 69.8$; $Fe = 8.49$; $Cl = 21.54$ per cent.

The *stannichloride*, prepared from benzanthrone (1 gram), acetic acid (15 c.c.), and fuming stannic chloride (1 gram), gave in a similar way a deposit of bright red needles, which when dry had a scarlet appearance. As the substance is apt to darken and become viscid when dried at 100° while moist with acetic acid, it was preferably submitted to a preliminary treatment in a vacuum.

Found: $C_{17}H_{10}O = 64.23$, 64.24 .

$(C_{17}H_{10}O)_2SnCl_4$ requires $C_{17}H_{10}O = 63.8$ per cent.

The *platinichloride* separates at once as a brick-red, semi-crystalline deposit, and this is also readily dissociated by water.

Found: $C_{17}H_{10}O = 53.4$; $Pt = 22.85$.

$(C_{17}H_{10}O)_2H_2PtCl_6$ requires $C_{17}H_{10}O = 52.88$; $Pt = 22.42$ per cent.

Having thus ascertained that benzanthrone readily yields salts of this character, it appeared interesting to study the behaviour of one or other of its hydroxy-derivatives in this respect, and certain of these are briefly described in the patent literature (Badische Anilin- & Soda-Fabrik, D.R.-P. 187495). Whereas benzanthrone is prepared by the action of glycerol and sulphuric acid on anthranol, the hydroxybenzanthrone are obtained in a similar way from the hydroxyanthranols, and that which is described as being produced from the 2-hydroxy-compound was selected at first for experiment. Following the directions given

for the preparation of this compound, the product consisted of a greenish-black powder, and could not, apparently, be crystallised. It was ascertained, however, that if a concentrated alcoholic extract of the material is poured into much ether, the main impurity separates as a dark-coloured, viscid mass, and that when the clear liquid, well washed with water, was evaporated, the hydroxy-compound remains as nodules in a comparatively pure form. For complete purification it was acetylated, and the crystals obtained by diluting the acetic anhydride solution with alcohol were recrystallised from a mixture of alcohol and acetic acid until they possessed the correct melting point of $200-201^{\circ}$.

When, for the purpose of hydrolysis, the acetyl compound, dissolved in boiling acetic acid, was treated with a few drops of sulphuric acid, scarlet needles, evidently the *sulphate* of the hydroxybenzanthrone, soon separated. These were collected, washed with acetic acid, and dried at 100° .

Found: C=59.04; H=3.37.

$C_{17}H_{10}O_2, H_2SO_4$ requires C=59.30; H=3.48 per cent.

On treatment with water, the sulphate is at once converted into the free hydroxybenzanthrone, a substance which is not readily crystallised, although from nitrobenzene it could be obtained as minute, microscopic needles.

Employing the haloid acids for the hydrolysis of the acetyl compound, oxonium salts could not be isolated.

Methoxybenzanthrone was readily obtained by suspending the hydroxybenzanthrone in methyl alcohol and adding methyl sulphate and methyl-alcoholic potassium hydroxide until no colour change was produced by the latter. It was isolated from the solution by means of water, washed with dilute alkali, and purified by crystallisation, first from alcohol and subsequently from benzene. The fine, yellow needles obtained in this way melted at $198-199^{\circ}$, and dissolved in both nitric and sulphuric acids, with the formation of green, fluorescent liquids.

Found: C=83.27; H=4.6.

$C_{18}H_{12}O_2$ requires C=83.07; H=4.6 per cent.

When a boiling acetic acid solution of methoxybenzanthrone is treated with a little sulphuric acid, fine, scarlet needles of the *sulphate* separated, and these were collected and washed with acetic acid.

Found: $C_{18}H_{12}O_2=72.02$; S=8.79.

$C_{18}H_{12}O_2, H_2SO_4$ requires $C_{18}H_{12}O_2=72.62$; S=8.93 per cent.

The *hydrobromide* and *hydrochloride* were obtained in a similar

manner as red needles, but, being unstable at 100°, were not submitted to analysis.

The *ferrichloride*, prepared by means of anhydrous ferric chloride and acetic acid without using hydrochloric acid,* separated immediately in fine, red needles. These, after being collected while hot and washed with acetic acid, formed a maroon-coloured

* The formation of the metallic oxonium salts here described is interesting as addition of hydrochloric acid in these cases is unnecessary and indeed objectionable, at least in the case of its aqueous solution. That required for reaction evidently originates from the conversion in part of the metallic chloride by means of the acetic acid either into acetate or chloride-acetate. That such a method of procedure is generally adaptable for this purpose appeared likely and experiment has shown that it can be successfully employed for the preparation of oxonium salts of this character from certain xanthone and flavone derivatives. Thus euxanthone diethyl ether in boiling acetic acid solution gives a *platinichloride*, as an orange-coloured, glistening mass of flat needles or leaflets readily dissociated in contact with warm water.

Found: Pt=19.92.

$(C_{17}H_{16}O_4)_2H_2PtCl_6$ requires Pt=19.93 per cent.

The *ferrichloride* consists of long, orange-yellow needles.

Found: $C_{17}H_{16}O_4$ =58.7; Cl=29.39.

$C_{17}H_{16}O_4 \cdot HFeCl_4$ requires $C_{17}H_{16}O_4$ =58.79; Cl=29.39 per cent.

Apigenin triethyl ether ferrichloride forms orange-yellow needles, somewhat soluble in hot acetic acid.

Found: $C_{21}H_{22}O_6$ =78.02.

$(C_{21}H_{22}O_6)_2HFeCl_4$ requires $C_{21}H_{22}O_6$ =78.05 per cent.,

and the *platinichloride* separates in minute needles of a similar colour.

Found: Pt=17.33.

$(C_{21}H_{22}O_6)_2H_2PtCl_6$ requires Pt=17.44 per cent.

Luteolin tetraethyl ether platinichloride is first deposited in the amorphous condition, but this gradually becomes crystalline when the boiling is continued for a short period.

Found: Pt=16.5.

$(C_{23}H_{26}O_6)_2H_2PtCl_6$ requires Pt=16.18 per cent.

Myricetin hexaethyl ether platinichloride separates in glistening, orange-coloured, rectangular plates.

Found: Pt=14.15.

$(C_{27}H_{34}O_8)_2H_2PtCl_6$ requires Pt=14.11 per cent.

Luteolin tetraethyl ether ferrichloride, (a) evidently $(C_{23}H_{26}O_6)_2HFeCl_4$, and the corresponding *myricetin* salt, (b) $(C_{27}H_{34}O_8)_2HFeCl_4$, both crystallise in orange-coloured needles, but, being somewhat soluble in acetic acid, hardly separate until the solution is cold. On this account these and other readily soluble compounds of the same character could not be isolated in a completely pure condition owing to the simultaneous deposition at this temperature of a trace of uncombined ferric salt. The yields of the regenerated ethyl ether, obtained by means of water were thus too low.

Found: (a) $C_{23}H_{26}O_6$ =76.8. Calc. 80.0 per cent.

(b) $C_{27}H_{34}O_8$ =67.5. Calc. 83.0 per cent.

glistening mass, and were readily decomposed in contact with water.

Found: $C_{18}H_{12}O_2 = 72.40$.

$(C_{18}H_{12}O_2)_3.HFeCl_4$ requires $C_{18}H_{12}O_2 = 72.32$ per cent.

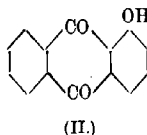
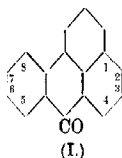
The *platinchloride*, similarly obtained, was scarlet.

Found: Pt = 21.26.

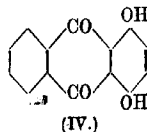
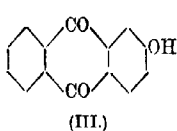
$(C_{18}H_{12}O_2)_2.H_2PtCl_6$ requires Pt = 20.97 per cent.

When methoxybenzanthrone dissolved in acetic acid was treated with chromic acid, an energetic reaction occurred, and by adding water to the solution, a small amount of a crystalline precipitate separated. This was collected, digested with hot dilute ammonia, and the extract neutralised with acid. On keeping, colourless, hair-like needles were deposited, and these, on heating, sintered at 265° and melted at 274 — 275° with evolution of gas. It at first suggested itself that this compound, which is evidently a *m*-methoxyanthraquinone-*o*-carboxylic acid, would be of service for ascertaining the position, apparently unknown, of the hydroxyl group in this and other hydroxybenzanthrones. Such an idea was, however, abandoned, as no account could be found in the literature of *m*-hydroxyanthraquinone-*o*-carboxylic acids, prepared by other methods, which might be identical or otherwise with the acid in question. Again, the yield of the latter was far from satisfactory.

In considering the constitution of this hydroxybenzanthrone derived from 2-hydroxyanthranol, four distinct positions, namely, 2, 3, 6, 7 (I), for the hydroxyl group at first appear applicable.



On the other hand, as it seems certain that the benzanthrone condensation proceeds similarly in the case of other hydroxyanthranols, the matter is in reality less complex. Thus the fact that 1-hydroxyanthraquinone (II) or the corresponding anthranol yields, according to the literature (*loc. cit.*), an hydroxybenzanthrone of



very similar properties to that derived from 2-hydroxyanthraquinone (III), renders the position 2 impracticable for the hydroxyl group present in the latter. Again, by a similar reasoning, the position 3 is not applicable, in that a dihydroxybenzanthrone can be prepared also from quinizarin (IV) or its leuco-compound (*loc. cit.*). Such being the case, the hydroxybenzanthrone under discussion, originating from 2-hydroxyanthranol, must contain the hydroxyl group in the position 6 or 7.

It appeared possible that a solution of this question might be arrived at from a study of the *o*-dihydroxybenzanthrone which has been obtained by the action of glycerol and sulphuric acid on deoxyalizarin (the anthranol corresponding with alizarin), and the examination of this compound was also of interest in that only a meagre account of its properties is to be found in the patent literature (*loc. cit.*).

The product, obtained in the usual manner by the interaction of deoxyalizarin, glycerol, and sulphuric acid, which consisted of a black, resinous powder, was extracted with alcohol, the extract evaporated to a small bulk, and poured into much ether. The clear liquid, decanted from a deposit of tarry impurity, was repeatedly washed with water and evaporated to dryness. The residue, which consisted of crystalline specks admixed with resinous matter, was triturated two or three times with a little ether, collected, and washed with the same solvent. The dull reddish-orange product was now digested with boiling acetic anhydride, the solution diluted with alcohol, and, after keeping overnight, the crystals which had then separated were collected and recrystallised from acetone.

Found: C=73.08; H=4.27.

$C_{21}H_{14}O_5$ requires C=72.83; H=4.05 per cent.

This *diacetoxybenzanthrone*, which has not been previously described, consists of pale yellow needles melting at 199—201°.

When a boiling solution of this compound in acetic acid is treated with sulphuric acid, the liquid becomes blood-red, and dark maroon needles of the *sulphate* of dihydroxybenzanthrone soon separate. These, when dry, appear almost black and closely resemble naphthazarin in appearance. In contact with water, they are slowly decomposed, being converted into minute, orange-red needles of the dihydroxy-compound.

Found: $C_{17}H_{10}O_5$ =72.02; S=8.79.

$C_{17}H_{10}O_5 \cdot H_2SO_4$ requires $C_{17}H_{10}O_5$ =72.77; S=8.88 per cent.

The *hydrobromide*, which is obtained in a similar way from the acetyl compound, separates in glistening, hair-like needles of a

deep maroon colour. On heating at 100° , it is slowly decomposed, and was therefore analysed indirectly by decomposing the product still moist with acetic acid by means of water, and estimating the regenerated dihydroxy-compound and the hydrobromic acid thus produced.

Found: 0.6495 gram of $C_{17}H_{10}O_3$, which corresponds with 0.8563 gram of $C_{17}H_{10}O_3 \cdot HBr$, and bromine equivalent to 23.28 per cent. of the latter. Theory requires $Br = 23.32$ per cent.

The *hydrochloride* and *hydriodide* were also prepared. These closely resembled the hydrobromide, but were not analysed.

The dihydroxybenzanthrone obtained by the hydrolysis of the acetyl derivative crystallised from alcohol, in which it is sparingly soluble, in minute, orange-red plates or leaflets, melting and decomposing at about $309-310^{\circ}$.

Found: $C = 78.1$; $H = 4.07$.

$C_{17}H_{10}O_3$ requires $C = 77.86$; $H = 3.81$ per cent.

This compound, for which the name *benzalizarin* is suggested, and is here referred to as such, resembles alizarin itself in many of its properties. It is soluble in concentrated sodium hydroxide solution with a pure blue colour, and this, on dilution with much water, gradually becomes dull violet, and finally brown, owing to oxidation. Addition of barium chloride to the blue alkaline solution causes the precipitation of the barium compound as a violet powder. Sulphuric acid dissolves it with a crimson, nitric acid with a bluish-violet, and alcoholic ferric chloride with a yellowish-brown, tint. Dyeing experiments, employing mordanted woollen cloth, indicated that benzalizarin dyes with this material shades which, with the exception of that given by the iron mordant, are identical in character with those given by alizarin itself, although they possess a slightly more orange tint.

	Cr.	Al.	Sn.	Fe.
Alizarin	Maroon.	Dull orange-red.	Bright reddish-orange.	Dull bluish-maroon.
Benzalizarin ...	Browner maroon.	Dull reddish-orange.	Bright orange.	Brownish-black.

The methylation of benzalizarin by means of methyl iodide and alkali was now studied in the hope that insight would thus be gained as to the exact position of its hydroxyl groups. Although it was at one time considered that by the use of these reagents it was not possible to methylate an hydroxyl group in the ortho-position with respect to a carbonyl group, this, at least in the case of colouring matters of the xanthone and flavone types, has now been shown to be incorrect (T., 1913, 103, 1632). On the other hand, there is no doubt that the carbonyl group does here exert

some steric hindrance, and in any case methylation of the hydroxyl group adjacent thereto is not effected except by using a considerable excess of iodide and alkali.

A mixture of benzalizarin (2 grams), methyl alcohol (30 c.c.), and methyl iodide (12 c.c.) was heated to boiling, and a solution of 2.5 grams of potassium hydroxide in methyl alcohol added drop by drop during some hours. Crystals, evidently of the monomethyl ether, soon separated, but these dissolved as the operation proceeded. After two days, the excess of methyl iodide was removed, and the crystals which separated were collected, washed with water, and recrystallised from acetone, employing animal charcoal.

Found: C=78.5; H=4.7; Me=10.1.

$C_{17}H_8O(OMe)_2$ requires C=78.62; H=4.82; Me=10.30 per cent.

It was found necessary to carry out the Zeisel determination in two stages (*a* and *b*), owing to the fact that the demethylated benzalizarin, even in the presence of acetic anhydride, separated as a spongy, colloidal mass, and enveloped a certain amount of unattacked or partly attacked substance. Thus, after two and a-half hours' digestion, methyl iodide ceased to be evolved, and the product, washed with sulphurous acid, dried, and ground, was again submitted to the action of hydriodic acid.

Found: (*a*) Me=9.13; (*b*) Me=0.97 per cent.

The regenerated benzalizarin, when acetylated, gave the acetyl compound, melting at 199–201°.

In this first experiment, although obviously an excess of alkali was employed, the reaction appeared to be at an end when less than half the amount had been added, and a second trial was now carried out in the same way, but using a solution of only 1 gram of commercial stick potassium hydroxide* in methyl alcohol. The product, isolated as in the former instance, weighed 2.02 grams, and only a trace of partly methylated substance soluble in alkali was present.

Dimethoxybenzanthrone crystallises from acetone in yellow needles melting at 139–141°, and is soluble in sulphuric acid with an orange-red colour devoid of fluorescence. It readily yields oxonium salts, and of these the *sulphate*, which crystallises in scarlet needles, was not analysed, owing to lack of material.

The *platinichloride* separates from acetic acid in small, red, glistening prisms.

Found: Pt=19.91.

$(C_{19}H_{14}O_3)_2PtCl_6$ requires Pt=19.70 per cent.

* The theoretical amount of pure potassium hydroxide required was 0.85 gram.

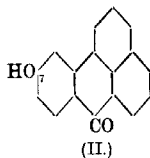
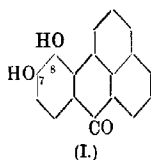
The *ferrichloride* consists of glistening, red needles.

Found: $C_{19}H_{14}O_3 = 74.34$.

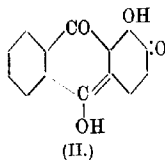
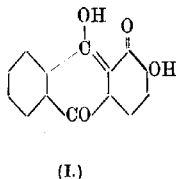
$(C_{19}H_{14}O_3)_2 \cdot HFeCl_4$ requires $C_{19}H_{14}O_3 = 74.45$ per cent.

For the sake of comparison with benzalizarin, alizarin itself was submitted to the action of methyl iodide under similar conditions to those given above, with the result that, as was to be anticipated, little or no methylation occurred, only a small amount of mono-methyl ether being thus produced.

There is, accordingly, considerable difference between the behaviour of these two colouring matters in this respect, and there is strong probability, therefore, that as benzalizarin can be so readily methylated with methyl iodide, it cannot contain an hydroxyl group in the ortho-position with respect to the carbonyl. It will thus have the constitution (I), and from this the position of the hydroxy-group in the hydroxybenzanthrone (II) discussed in this paper will naturally follow.



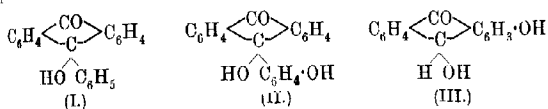
Such being the case, it is very interesting that the dyeing properties of benzalizarin should so closely resemble those of alizarin. The latter are assumed to result from its possession of two hydroxyl groups in the ortho-position relatively to one another, one of which is adjacent to a carbonyl group. Based on this view, an ortho-quinonoid structure (I) for the alizarin lakes has been proposed (T., 1899, 75, 433), but in case the constitution of benzalizarin given above receives full support, a para-quinonoid form (II) would prove more applicable.



The latter has, indeed, been previously suggested for the blue alkali salts of this colouring matter. The fact that benzanthrone and its hydroxy-derivatives give salts of an intensely coloured nature is interesting, in that, as these are presumably oxonium

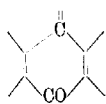
compounds, their formation can only originate from the oxygen of the carbonyl group. Such a reaction is more usually associated with substances containing pyrone and analogous nuclei, and in these instances it is usually assumed that it is the basicity of the pyrone oxygen that comes into play. Salts of this character do not, for instance, appear to be producible from acetophenone, benzophenone, or their hydroxy-derivatives. On the other hand, when the carbonyl group forms part of a six-membered ring, as in benzanthrone, there is apparently further evidence that its basicity is thus increased. Thus, in case solution of a compound of this nature in sulphuric acid is accompanied by an intense colour, and addition of water precipitates the unchanged substance, it is reasonable to suspect the formation of an oxonium salt.*

Whether the latter condition is fulfilled in all the substances here cited is, however, uncertain, but presuming this to be so, three compounds described by Baeyer, namely, phenylhydroxyanthranol (I), hydroxyphenylhydroxyanthranol (II), and phenolphthalidin (III) (*Annalen*, 1880, **202**, 58), which contain a nucleus

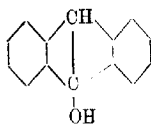


(IV) similar to that present in benzanthrone, are interesting, as they are described as yielding in this way purple, red, and purplish-violet colorations respectively.

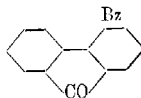
Such a property is not shown by anthranol itself, and this may be due to the fact that in sulphuric acid solution it is present entirely in the enolic condition (V). Possibly, again, compounds



(IV.)



(V.)



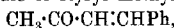
(VI.)

containing the carbonyl group in a five-membered ring may be reactive, for benzoylfluorenone (VI) (Götz, *Monatsh.*, 1902, **23**, 30) dissolves in sulphuric acid with a reddish-yellow tint.

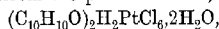
Such colour changes are also given by compounds in which the carbonyl group is present in an open chain and adjacent to an unsaturated linking, and is, indeed, the property of numerous

* It is singular, however, that the hydrocarbon carotene, $\text{C}_{40}\text{H}_{56}$, dissolves in sulphuric acid with an indigo-blue coloration.

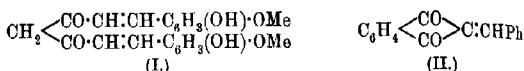
styryl methyl ketone (chalkone) derivatives. Moreover, oxonium salt-formation in the case of styryl methyl ketone,



itself seems certain, in that Baeyer and Villiger (*Ber.*, 1901, 34, 2695) obtained therefrom the platinichloride,



in the form of yellow prisms. Curcumin (I), again, as is well



known, dissolves in sulphuric acid with an intense red tint, whereas colour changes of this character are also given by certain derivatives of benzylideneindandione (II). An investigation is in progress with the object of obtaining more definite information as to the formation of oxonium salts in the case of these and allied compounds.

In connexion, again, with the present investigation, experiments were carried out to determine whether compounds of this character could be prepared from alizarin dimethyl ether, but, employing acetic acid for this purpose, no evidence of oxonium salt-formation could be observed either with mineral acids or anhydrous metallic compounds. On the other hand, it has been found that if rufigallol is stirred into concentrated sulphuric acid, maroon-coloured, glistening, prismatic needles soon appear, which evidently consist of a sulphate. These may be collected on glass wool, but all attempts to remove adherent sulphuric acid without simultaneously dissociating the substance have hitherto been unsuccessful. Glacial acetic acid alone or admixed with acetic anhydride rapidly causes the production of bright red rufigallol, and even sulphuryl chloride gradually effects the same colour-change. It seems possible, however, that rufigallol methyl ether may furnish compounds of this character sufficiently stable for analysis, and experiments on this point are about to be undertaken.

Anthraquinone-1-carboxylic Acid.

As benzanthrone appeared to be a useful source of this acid for laboratory purposes, experiments were carried out in order to ascertain the best conditions for this purpose, and the following method was adopted.

A solution of 2 grams of benzanthrone in 20 c.c. of boiling acetic acid was slowly treated during three hours with a solution of 10 grams of commercial chromic acid in 20 c.c. of 50 per cent. acetic acid. The product, when diluted with hot water, deposited

crystals, and, after keeping overnight, these were collected. The filtrate, which contained some quantity of the anthraquinonecarboxylic acid in solution, was treated with sufficient sulphuric acid to convert the chromium into sulphate, evaporated to dryness, the residue extracted with water, and the crystals were collected. 0.091 Grams of the substance were thus isolated, which, however, contained chromium, and this was removed by treatment with 5 c.c. of sulphuric acid at 100° and subsequent precipitation with water. The product was dissolved in boiling dilute ammonia and the solution filtered, when, on acidification, the carboxylic acid was obtained in almost colourless needles melting at $286-288^{\circ}$, and weighing 1.8320 grams (Found: C=71.47; H=3.35. $C_{15}H_8O_4$ requires C=71.43; H=3.17 per cent.).

By recrystallisation from ten times its weight of nitric acid (D 1.42), and diluting the product with a little water, the preparation, which thus lost approximately 5 per cent. of its weight, melted at $291-292^{\circ}$.

Note on a Product of the Destructive Distillation of Sodium Anthraquinone- β -sulphonate.

Many years ago it was shown (A. G. and W. H. Perkin, T., 1885, 47, 679) that when sodium anthraquinone- β -sulphonate is destructively distilled, there is produced, in addition to some quantity of anthraquinone and 2-hydroxyanthraquinone, a small amount of an orange-coloured substance. To the latter the formula $C_{28}H_{14}O_6$ was then assigned, and from this, by progressive oxidation, two colourless compounds, represented as $C_{28}H_{14}O_7$ and $C_{14}H_6O_4$, could be obtained. A further investigation of this subject was contemplated from time to time, but for the lack of a suitable apparatus capable of dealing with a large amount of the sulphonate, this has until very recently remained in abeyance. Although originally unsuspected, it has been known for some time that the compound to which the formula $C_{28}H_{14}O_6$ was assigned contains a small amount of sulphur. As a consequence, there can be little doubt that its true formula is $C_{28}H_{14}O_6S$, and with this the carbon and hydrogen analyses given in the paper are in full agreement. It is likely that this substance is in reality a thiodianthraquinone, $(C_{14}H_6O_2)_2S$, and, should this be the case, the formulæ of its oxidation products will thus be $C_{28}H_{14}O_7S$ and $C_{28}H_{14}O_8S$, and their constitutions naturally follow. It is interesting to note that in its reaction with sulphuric acid and general properties the former compound closely resembles the thiodianthraquinone prepared by

the interaction of 2-chloroanthraquinone and 2-thiolanthraquinone (Farbenfabriken vorm. F. Bayer & Co., D.R.-P. 274357). The further examination of these compounds and the study of a similar product from sodium anthraquinone- α -sulphonate, are in progress.

This statement has appeared necessary on account of a brief allusion to these compounds in a paper by Scholl, Schwinger, and Dischendorfer (*Ber.*, 1919, **52**, [B], 2260), and the opinion, "Man kann sogar in Zweifel sein ob sie einheitliche Verbindungen in Händen gehabt haben," there given.

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LXXV.—*n*-Butyl Chloroformate and its Derivatives.

By FREDERICK DANIEL CHATTAWAY and EDOUARD SAERENS.

n-Butyl chloroformate, $\text{Cl}\cdot\text{CO}_2\cdot\text{C}_4\text{H}_9$, is best prepared by passing carbonyl chloride into cooled *n*-butyl alcohol until the calculated increase in weight is reached, and fractionally distilling the product.

It is difficult to separate the chloroformate from the unchanged *n*-butyl alcohol, and the yield is not large, as in the repeated fractional distillations necessary a considerable amount reacts with the alcohol to form di-*n*-butyl carbonate. If the first fractionations are slow, a distillate is frequently obtained which contains only this and *n*-butyl chloride.

n-Butyl chloroformate is a colourless, mobile liquid of a sharp, but pleasant, odour; the vapour attacks the eyes. It boils at $137.8^\circ/734.5$ mm., and has D_4^{25} 1.074 and n_D^{25} 1.417.

It is only slowly hydrolysed when heated with water, in which it appears to be insoluble:

0.2587 gave 0.2725 AgCl. $\text{Cl}=26.05$.

$\text{C}_4\text{H}_9\text{O}_2\text{Cl}$ requires $\text{Cl}=25.97$ per cent.

Di-*n*-butyl carbonate, $(\text{C}_4\text{H}_9)_2\text{CO}_3$, was originally prepared by Lieben and Rossi (*Annalen*, 1873, **165**, 112) by heating *n*-butyl iodide with silver carbonate. The quantity obtained was very small, as much Δ^a -butylene and di-*n*-butyl ether are produced in the reaction.

It is always formed in small amount during the fractionation in the preparation of *n*-butyl chloroformate, and is easily obtained in quantity by passing carbonyl chloride into hot *n*-butyl alcohol.

by boiling *n*-butyl chloroformate with about twice the equivalent amount of *n*-butyl alcohol, and fractionating to separate any unchanged alcohol and the *n*-butyl chloride formed. Di-*n*-butyl carbonate is a colourless, mobile liquid of a somewhat pleasant smell, which boils at 207°/745 mm.

When *n*-butyl chloroformate is heated with any alcohol, it gives the corresponding alkyl *n*-butyl carbonate. The isolation of these alkyl *n*-butyl carbonates in a pure state by fractional distillation is generally tedious, as both the dialkyl carbonate and di-*n*-butyl carbonate are formed as well as the mixed ester, otherwise their preparation offers no difficulty. To avoid so far as possible the actions by which these by-products are formed, it is best to add the equivalent amount of the alcohol to boiling *n*-butyl chloroformate.

Methyl n-butyl carbonate, $C_4H_9 \cdot O \cdot CO \cdot OMe$, is a colourless, mobile liquid having a sweet smell, somewhat recalling that of amyl acetate; it boils at 150.5°/745 mm.:

0.2154 gave 0.4301 CO_2 and 0.1769 H_2O . C=54.46; H=9.19.

$C_6H_{12}O_3$ requires C=54.50; H=9.15 per cent.

Ethyl n-butyl carbonate, $C_4H_9 \cdot O \cdot CO \cdot OEt$, is a colourless, mobile, sweet-smelling liquid, which boils at 168.5°/748 mm.:

0.1757 gave 0.3693 CO_2 and 0.1507 H_2O . C=57.32; H=9.60.

$C_7H_{14}O_3$ requires C=57.49; H=9.63 per cent.

n-Propyl n-butyl carbonate, $C_4H_9 \cdot O \cdot CO \cdot O \cdot C_3H_7$, is a colourless, mobile liquid having a pleasant smell, and boils at 187.5°/755 mm.:

0.1688 gave 0.3703 CO_2 and 0.1517 H_2O . C=59.83; H=10.05.

$C_8H_{16}O_3$ requires C=59.95; H=10.07 per cent.

n-Butyl chloroformate reacts very readily and energetically with ammonia and with amines to form *n*-butyl carbamates. In the case of ammonia, it is sufficient to shake vigorously the chloroformate with concentrated aqueous ammonia. With the amines it is best to add an ethereal solution of the base mixed with an equivalent amount of pyridine to an ethereal solution of the equivalent quantity of *n*-butyl chloroformate. The *n*-butyl carbamates are, as a rule, colourless, well-crystallised compounds readily soluble in alcohol or other ordinary organic solvents.

n-Butyl carbamate, $C_4H_9 \cdot O \cdot CO \cdot NH_2$, is very readily soluble in alcohol, and crystallises in long, colourless, flattened prisms, which melt at 54°:

0.1814 gave 0.3402 CO_2 and 0.1527 H_2O . C=51.14; H=9.42.

$C_5H_{11}O_2N$ requires C=51.24; H=9.47 per cent.

710 N-BUTYL CHLOROFORMATE AND ITS DERIVATIVES.

n-Butyl phenylcarbamate, $C_4H_9 \cdot O \cdot CO \cdot NHPh$, crystallises in long, colourless, flattened prisms, which melt at 65.5° :

0.2543 gave 0.6381 CO_2 and 0.1740 H_2O . $C = 68.43$; $H = 7.65$.

$C_{11}H_{15}O_2N$ requires $C = 68.35$; $H = 7.83$ per cent.

n-Butyl *o*-chlorophenylcarbamate, $C_4H_9 \cdot O \cdot CO \cdot NH \cdot C_6H_4Cl$, is an oily liquid boiling at $235-240^\circ/60$ mm., which does not solidify on keeping or when cooled in a freezing mixture:

0.3513 gave 0.2160 $AgCl$. $Cl = 15.21$.

$C_{11}H_{14}O_2NCl$ requires $Cl = 15.58$ per cent.

n-Butyl *p*-chlorophenylcarbamate crystallises in colourless, flattened, apparently rhombic, prisms, which melt at 72° :

0.2346 gave 0.1492 $AgCl$. $Cl = 15.73$.

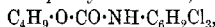
$C_{11}H_{14}O_2NCl$ requires $Cl = 15.58$ per cent.

n-Butyl 2:4-dichlorophenylcarbamate, $C_4H_9 \cdot O \cdot CO \cdot NH \cdot C_6H_3Cl_2$, crystallises in colourless, very slender prisms, which melt at 48° :

0.2070 gave 0.2261 $AgCl$. $Cl = 27.02$.

$C_{11}H_{13}O_2NCl_2$ requires $Cl = 27.06$ per cent.

n-Butyl 2:4:6-trichlorophenylcarbamate,



crystallises in slender, colourless prisms, which melt at 60° :

0.2236 gave 0.3252 $AgCl$. $Cl = 35.98$.

$C_{11}H_{12}O_2NCl_3$ requires $Cl = 35.88$ per cent.

n-Butyl *m*-bromophenylcarbamate, $C_4H_9 \cdot O \cdot CO \cdot NH \cdot C_6H_4Br$, crystallises in colourless, transparent, four-sided rhombic plates melting at 37.5° :

0.2425 gave 0.1669 $AgBr$. $Br = 29.29$.

$C_{11}H_{14}O_2NBr$ requires $Br = 29.38$ per cent.

n-Butyl *p*-bromophenylcarbamate crystallises in compact, colourless, rhombic prisms, which melt at 67° :

0.2424 gave 0.1670 $AgBr$. $Br = 29.32$.

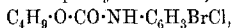
$C_{11}H_{14}O_2NBr$ requires $Br = 29.38$ per cent.

n-Butyl 2:4-dibromophenylcarbamate, $C_4H_9 \cdot O \cdot CO \cdot NH \cdot C_6H_3Br_2$, crystallises in very slender, silky, hair-like prisms, which melt at 61.5° :

0.2130 gave 0.2278 $AgBr$. $Br = 45.51$.

$C_{11}H_{13}O_2NBr_2$ requires $Br = 45.54$ per cent.

n-Butyl 2-chloro-4-bromophenylcarbamate,



crystallises in very slender, hair-like prisms, which melt at 52° :

0.1913 gave 0.2061 $AgCl + AgBr$. Calc.: 0.2066 $AgCl + AgBr$.

n-Butyl *p*-iodophenylcarbamate, $C_4H_9 \cdot O \cdot CO \cdot NH \cdot C_6H_4I$, crystallises in long, colourless prisms, which melt at 72° :

0.3048 gave 0.2232 AgI. $I = 39.58$.

$C_{11}H_{14}O_2NI$ requires $I = 39.78$ per cent.

n-Butyl *o*-tolylcarbamate, $C_4H_9 \cdot O \cdot CO \cdot NH \cdot C_6H_4Me$, crystallises in colourless, slender prisms, which melt at 45.5° :

0.2173 gave 0.5534 CO_2 and 0.1596 H_2O . $C = 69.45$; $H = 8.22$.

$C_{12}H_{17}O_2N$ requires $C = 69.51$; $H = 8.27$ per cent.

n-Butyl *p*-tolylcarbamate crystallises in stout, colourless prisms, which melt at 63° :

0.2345 gave 0.5983 CO_2 and 0.1722 H_2O . $C = 69.58$; $H = 8.21$.

$C_{12}H_{17}O_2N_2$ requires $C = 69.51$; $H = 8.27$ per cent.

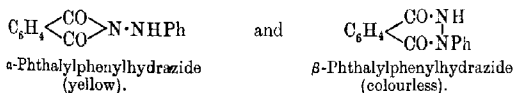
THE QUEEN'S COLLEGE,
OXFORD.

[Received, May 19th, 1920.]

LXXXVI.—Isomeric Phthalylhydrazides.

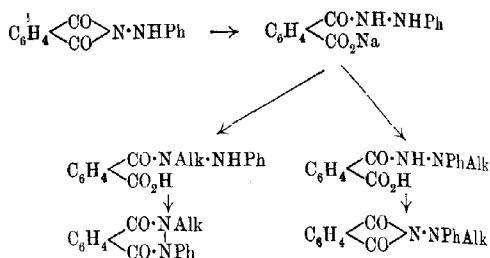
By FREDERICK DANIEL CHATTAWAY and WILLIAM TESH.

Two isomeric phthalylphenylhydrazides have been described, one yellow and crystallising in two enantiotropic modifications, the other colourless. The yellow compound has been much studied and the transition point of its polymorphs determined; its colourless isomeride has received less attention, and the conditions under which it is produced are still imperfectly understood. For convenience, the isomerides have been designated α - and β -phthalylphenylhydrazide, and the constitutions

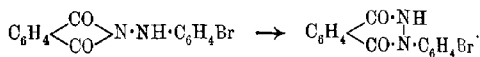


have, with some justification, been assigned to them.

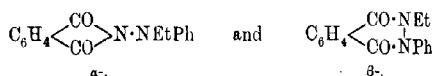
Pairs of isomerides similar in constitution and properties to these have been obtained by the action of alkyl iodides on the sodium salts of the phthalylhydrazinic acids, obtained by dissolving α -phthalylphenylhydrazide in an alcoholic solution of sodium ethoxide, for example:



Although the α -phthalylhydrazides undergo no noticeable transformation when heated in sealed tubes to temperatures below those at which decomposition and gas evolution occur, those having a hydrogen atom attached to the nitrogen atom carrying the aryl group are gradually transformed into the corresponding β -isomerides when heated to about 210° for some hours with glycerol or when boiled for a similar period with the equivalent amount of sodium ethoxide dissolved in alcohol, thus:



EXPERIMENTAL.

 α - and β -Phthalylphenylethylhydrazides,

α -Phthalylphenylhydrazide was dissolved in an alcoholic solution of an equivalent amount of sodium ethoxide, rather more than an equivalent amount of ethyl iodide added, and the mixture heated in a sealed tube to 120° for twelve hours. A brown mass was produced, which was dissolved in alcohol, and steam passed through to remove the solvent alcohol and an excess of ethyl iodide. The solid product remaining was dissolved in boiling alcohol, and, on cooling, yellow crystals of α -phthalylphenylethylhydrazide separated. The filtrate was concentrated and cooled, when β -phthalylphenylethylhydrazide crystallised in white needles. Each was then several times recrystallised from alcohol.

The yellow α -compound dissolves readily in boiling alcohol, and crystallises in long, yellow, flattened prisms melting at 134° :

0.2337 gave 21 c.c. N_2 (moist) at 15.8° and 764.5 mm. $\text{N} = 10.33$.

$\text{C}_{16}\text{H}_{14}\text{O}_2\text{N}_2$ requires $\text{N} = 10.52$ per cent.

The colourless β -compound is very readily soluble in boiling alcohol, and crystallises in colourless needles melting at 109° :

0.1979 gave 17.8 c.c. N_2 (moist) at 11.6° and 756 mm. $N=10.61$.

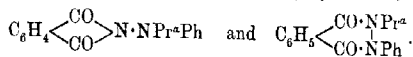
The yellow α -phthalylphenylethylhydrazide was also prepared by heating an alcoholic solution of α -phthalylphenylhydrazide with an equivalent amount of ethyl iodide in the presence of an equivalent amount of zinc oxide. In this experiment, none of the colourless compound was formed.

To establish the constitution of the yellow α -form, phenylethylhydrazine was prepared from monoethylaniline, and an alcoholic solution heated with phthalic anhydride.

The α -phthalylphenylethylhydrazide prepared in this way was identical with the yellow compound melting at 134° .

The β -phthalylphenylethylhydrazide (m. p. 109°), prepared as above, is certainly identical with that obtained by Hötte (*J. pr. Chem.*, 1887, [ii], **35**, 265) by heating ethyl iodide with a solution of β -phthalylphenylhydrazide in alcoholic potassium hydroxide. He describes it as crystallising in white needles melting at $105-106^{\circ}$. We have always, however, found the compound to melt at a slightly higher temperature, namely, 109° .

*α - and β -Phthalylphenyl-*n*-propylhydrazides,*



These compounds were prepared exactly as the ethyl compounds, by heating a slight excess of *n*-propyl iodide with a solution of phthalylphenylhydrazide in an alcoholic solution of sodium ethoxide for sixteen hours to $125-130^{\circ}$.

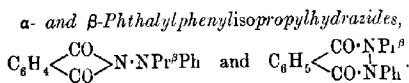
α -Phthalylphenyl-*n*-propylhydrazide is readily soluble in alcohol, and crystallises in bright yellow, small, irregular rhombs, which melt at 110° :

0.3126 gave 26.5 c.c. N_2 (moist) at 13.8° and 760 mm. $N=9.96$.

$C_{17}H_{16}O_2N_2$ requires $N=10.0$ per cent.

β -Phthalylphenyl-*n*-propylhydrazide dissolves readily in alcohol, and crystallises in long, slender, colourless, six-sided prisms, which melt at 75° :

0.2935 gave 25.2 c.c. N_2 (moist) at 11.6° and 750 mm. $N=10.15$.



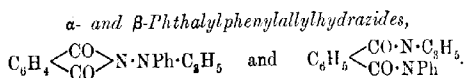
These were obtained in a similar manner to the normal compounds.

α-Phthalylphenylisopropylhydrazide is readily soluble in alcohol, and crystallises in bright yellow, rhombic plates, which melt at 142°:

0.3161 gave 27.8 c.c. N₂ (moist) at 17.2° and 750 mm. N=10.07,
 C₁₇H₁₆O₂N₂ requires N=10.0 per cent.

β-Phthalylphenylisopropylhydrazide dissolves readily in alcohol, and crystallises in slender, colourless, four-sided prisms, which melt at 103°:

0.3176 gave 0.8510 CO₂ and 0.1657 H₂O. C=73.07; H=5.79,
 0.2218 „ 19.4 c.c. N₂ (moist) at 17° and 752 mm. N=10.04.
 C₁₇H₁₆O₂N₂ requires C=72.81; H=5.75; N=10 per cent.



These were prepared in a similar manner to the previously described compounds, the action with the allyl iodide being especially vigorous, heating for half an hour only on the water-bath being required to complete it.

α-Phthalylphenylallylhydrazide is readily soluble in alcohol, and crystallises in bright yellow prisms, which melt at 142°:

0.3068 gave 26 c.c. N₂ (moist) at 10° and 747.5 mm. N=9.97
 C₁₇H₁₄O₂N₂ requires N=10.07 per cent.

β-Phthalylphenylallylhydrazide dissolves very readily in alcohol and crystallises in slender, colourless prisms, which melt at 90°:

0.2162 gave 18 c.c. N₂ (moist) at 13° and 756 mm. N=9.79.

Phthalylphenyltrimethylenebishydrazide.

Ninety grams of phthalylphenylhydrazide were dissolved in a solution of 6 grams of sodium in 200 c.c. of alcohol, and heated with 40.4 grams of trimethylene bromide on a water-bath for six hours.

The sodium bromide which separated was filtered off, 4 grams of sodium dissolved in alcohol were added, and the mixture was again heated for two hours. On adding water, *phthalylphenyltri*

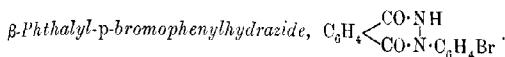
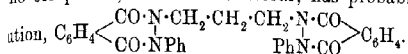
*methylenebis*hydrazide separated as a white solid. It was recrystallised from hot alcohol, in which it is readily soluble, and separated in long, colourless, slender prisms melting at 187°:

0.1017 gave 0.2703 CO₂ and 0.0439 H₂O. C=72.48; H=4.79.

0.1475 „ 13 c.c. N₂ (moist) at 8° and 760 mm. N=10.64.

C₃₁H₂₄O₄N₄ requires C=72.1; H=4.65; N=10.8 per cent.

The compound, from its behaviour, has probably the bis-β-con-



Phthalyl-*p*-bromophenylhydrazide has already been obtained the interaction of phthalic anhydride and *p*-bromophenylhydrazide at 100°. It crystallises from hot alcohol in bright yellow, monoclinic prisms, which melt at 206° (Chattaway and Wunsch, T., 1, 99, 2260).

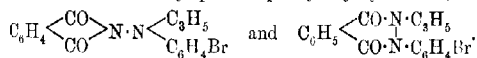
This compound was transformed into the sodium salt of the omeride by heating with the equivalent quantity of sodium oxide in alcoholic solution in a sealed tube to 100° for eight hrs. On adding hydrochloric acid to the solution, the omeride separated. It was recrystallised from hot alcohol, in which it is moderately easily soluble, and separated in fine, white plates melting at 252°:

0.1149 gave 0.2270 CO₂ and 0.0315 H₂O. C=53.00; H=3.04.

0.1206 „ 8.9 N₂ (moist) at 9° and 760 mm. N=8.87.

C₁₄H₉O₂N₂Br requires C=53.0; H=2.84; N=8.83 per cent.

α- and *β*-Phthalyl-*p*-bromophenylallylhydrazides,



These compounds were prepared similarly to the corresponding allyl derivatives, by heating allyl iodide with *α*-phthalyl-*p*-bromophenylhydrazide dissolved in an equivalent amount of alcoholic sodium ethoxide on a water-bath for seven to eight hours.

Phthalyl-*p*-bromophenylallylhydrazide is readily soluble in hot alcohol, and crystallises in bright yellow, slender, four-sided prisms, which melt at 118°:

0.2893 gave 0.1453 AgBr. Br=21.37.

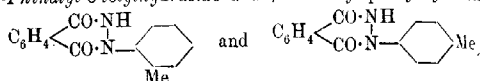
C₁₇H₁₃O₂N₂Br requires Br=21.45 per cent.

Phthalyl-*p*-bromophenylallylhydrazide is moderately soluble in

hot alcohol, and crystallises in long, very thin, colourless needles melting at 129°:

0.0948 gave 0.0485 AgBr. Br = 21.71.

β-Phthalyl-o-tolylhydrazide and *β-Phthalyl-p-tolylhydrazide*,



α-Phthalyl-o-tolylhydrazide and *α-phthalyl-p-tolylhydrazide* have already been prepared by the interaction of phthalic anhydride and the corresponding tolyhydrazines; the former crystallises in small tabular, monoclinic, bright orange crystals, which melt at 198°, the latter in long, deep orange, prismatic crystals, which melt at 196° (Chattaway and Wünsch, *loc. cit.*). They are both easily converted into the corresponding *β*-isomerides by heating in a sealed tube to 100° for eight hours with an alcoholic solution of the equivalent amount of sodium ethoxide, and precipitating by acid.

β-Phthalyl-o-tolylhydrazide is moderately readily soluble in hot alcohol, and separates in colourless, compact crystals, which melt at 207°:

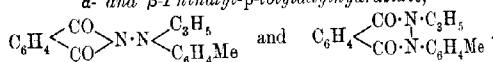
0.2188 gave 20.8 c.c. N₂ (moist) at 13° and 751.5 mm. N = 11.16

C₁₅H₁₂O₂N₂ requires N = 11.11 per cent.

β-Phthalyl-p-tolylhydrazide dissolves moderately readily in hot alcohol, and crystallises in very slender, colourless prisms, which melt at 225°:

0.1438 gave 13.8 c.c. N₂ (moist) at 10° and 748 mm. N = 11.3

α- and β-Phthalyl-p-tolylallylhydrazides,



These were prepared similarly to the corresponding phenyl compounds.

α-Phthalyl-p-tolylallylhydrazide is very readily soluble in hot alcohol, and crystallises in bright yellow, irregular, rhombic plates which melt at 87°:

0.2095 gave 17.6 c.c. N₂ (moist) at 17° and 764 mm. N = 9.75

C₁₈H₁₆O₂N₂ requires N = 9.6 per cent.

β-Phthalyl-p-tolylallylhydrazide is very readily soluble in hot alcohol, and crystallises in colourless, six-sided prisms, which melt at 102°:

0.1668 gave 13.8 c.c. N₂ (moist) at 16° and 763 mm. N = 9.61

Acyl Derivatives of the Phthalylhydrazides.

All the phthalylhydrazides containing hydrogen attached to nitrogen readily form colourless acyl derivatives. Several of these have been prepared from various members of the α - and β -series hydrazides by heating them for some hours with formic acid, acetic, propionic or *n*-butyric anhydride, or benzoyl chloride in sealed tubes.

α -Phthalylformylphenylhydrazide, $C_8H_4O_2:N \cdot NPh \cdot CHO$, crystallises from alcohol in small, colourless rhombs melting at 185° :

0.2418 gave 21.8 c.c. N_2 (moist) at 16° and 759 mm. $N=10.48$.
 $C_{15}H_{10}O_3N_2$ requires $N=10.52$ per cent.

α -Phthalylacetylphenylhydrazide, $C_8H_4O_2:N \cdot NPh \cdot Ac$, crystallises from alcohol in colourless, flattened, four-sided prisms melting at 185° :

0.2035 gave 17.5 c.c. N_2 (moist) at 18° and 759 mm. $N=9.86$.
 $C_{16}H_{12}O_3N_2$ requires $N=10.0$ per cent.

β -Phthalylacetylphenylhydrazide, $C_6H_4 \begin{matrix} \diagup CO \cdot NAc \\ \diagdown CO \cdot NPh \end{matrix}$, crystallises from alcohol in colourless, prismatic crystals melting at 127° :

0.2256 gave 20.1 c.c. N_2 (moist) at 18° and 752 mm. $N=10.16$.
 $C_{16}H_{12}O_3N_2$ requires $N=10.0$ per cent.

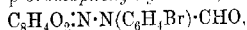
α -Phthalylpropionylphenylhydrazide, $C_8H_4O_2:N \cdot NPh \cdot COEt$, crystallises from alcohol in colourless, four-sided plates melting at 148° :

0.2481 gave 20.3 c.c. N_2 (moist) at 16° and 759 mm. $N=9.51$.
 $C_{17}H_{14}O_3N_2$ requires $N=9.52$ per cent.

β -Phthalyl-*n*-butyrylphenylhydrazide, $C_8H_4O_2:N \cdot NPh \cdot CO \cdot C_3H_7$, crystallises from alcohol in short, white prisms melting at 126° :

0.2312 gave 17.8 c.c. N_2 (moist) at 17° and 748 mm. $N=8.78$.
 $C_{18}H_{16}O_3N_2$ requires $N=9.09$ per cent.

β -Phthalylformyl-*p*-bromophenylhydrazide,

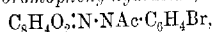


crystallises from alcohol in colourless, six-sided prisms melting at 130° :

0.2792 gave 0.1536 AgBr. $Br=23.4$.

$C_{15}H_9O_3N_2Br$ requires $Br=23.2$ per cent.

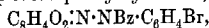
β -Phthalylacetyl-*p*-bromophenylhydrazide,



crystallises from alcohol in colourless prisms melting at 166° :

0.1763 gave 0.0914 AgBr. $Br=22.06$.

$C_{16}H_9O_3N_2Br$ requires $Br=22.28$ per cent.

α-Phthalylbenzoyl-p-bromophenylhydrazide,

crystallises from alcohol in colourless, small rhombs melting at 166°:

0.2032 gave 0.0920 AgBr. Br=19.27.

$\text{C}_{21}\text{H}_{13}\text{O}_3\text{N}_2\text{Br}$ requires 19.0 per cent.

α-Phthalylformyl-o-tolylhydrazide, $\text{C}_8\text{H}_4\text{O}_2\cdot\text{N}\cdot\text{N}(\text{C}_6\text{H}_4\text{Me})\cdot\text{CHC}$

crystallises from alcohol in colourless, long, slender needles melting at 112°:

0.1472 gave 12.5 c.c. N_2 (moist) at 10° and 754 mm. N=10.0.

$\text{C}_{10}\text{H}_{12}\text{O}_3\text{N}_2$ requires N=10.0 per cent.

α-Phthalylacetyl-o-tolylhydrazide, $\text{C}_8\text{H}_4\text{O}_2\cdot\text{N}\cdot\text{Nac}\cdot\text{C}_6\text{H}_4\text{Me}$

crystallises from alcohol in colourless, four-sided prisms melting at 161°:

0.2339 gave 19.3 c.c. N_2 (moist) at 18° and 759 mm. N=9.51.

$\text{C}_{17}\text{H}_{14}\text{O}_3\text{N}_2$ requires N=9.52 per cent.

α-Phthalylbenzoyl-o-tolylhydrazide, $\text{C}_8\text{H}_4\text{O}_2\cdot\text{N}\cdot\text{NBz}\cdot\text{C}_6\text{H}_4\text{Me}$

crystallises from alcohol in colourless, stout, rhombic prisms melting at 151°:

0.2392 gave 16.2 c.c. N_2 (moist) at 17° and 760 mm. N=7.85.

$\text{C}_{22}\text{H}_{16}\text{O}_3\text{N}_2$ requires N=7.87 per cent.

α-Phthalylformyl-p-tolylhydrazide crystallises from alcohol in long, colourless prisms melting at 180°:

0.1776 gave 15.4 c.c. N_2 (moist) at 18° and 759.5 mm. N=9.9.

$\text{C}_{16}\text{H}_{12}\text{O}_3\text{N}_2$ requires N=10.0 per cent.

α-Phthalylacetyl-p-tolylhydrazide crystallises from alcohol in colourless, four-sided prisms melting at 151°:

0.1872 gave 15.2 c.c. N_2 (moist) at 17° and 759 mm. N=9.4.

$\text{C}_{17}\text{H}_{14}\text{O}_3\text{N}_2$ requires N=9.52 per cent.

α-Phthalylbenzoyl-p-tolylhydrazide crystallises from alcohol in colourless prisms melting at 135°:

0.1255 gave 8.4 c.c. N_2 (moist) at 10° and 752 mm. N=7.92.

$\text{C}_{22}\text{H}_{16}\text{O}_3\text{N}_2$ requires N=7.87 per cent.

Transformation of α- into β-Phthalylphenylhydrazide.

Although when the phenylhydrazinic acid formed by the combination of phenylhydrazine with phthalic anhydride loses water the coupling probably takes place in two directions, leading to the production of the *α*- and of the *β*-isomeride, the amount of the latter formed at temperatures between 100° and 170° is so small as to be unrecognisable.

The decomposition of the α -compound into phthalanil, nitrogen, and ammonia (compare Chattaway, Cumming, and Wilsdon, T., 1911, **99**, 1951), which becomes vigorous at temperatures above 300° , takes place to a small extent at the lower temperature also, and it is very difficult to separate the constituents of the small, viscous residue left on evaporating the mother liquor from which the α -phthalylphenylhydrazide has crystallised.

That neither α - nor β -phthalylphenylhydrazide is transformed appreciably into the other when heated alone was shown by heating a few grams of each in sealed tubes to 250° for six hours. On once crystallising the solidified mass, the original compound was obtained in a pure state.

Transformation of α - into β -Phthalylphenylhydrazide by Heating with an Alcoholic Solution of Sodium Ethoxide.

Sodium (2.3 grams) was dissolved in 100 c.c. of alcohol, 23.8 grams of α -phthalylphenylhydrazide were added, and the whole was heated on a water-bath for seven hours. After dilution with water, the filtered liquid was acidified with hydrochloric acid, and the white substance which separated was recrystallised from alcohol. It separated in colourless, compact, irregular crystals, which melted at 211 – 212° (Found: C=70.65; H=4.40; N=11.50. $C_{14}H_{10}O_2N_2$ requires C=70.59; H=4.20; N=11.77 per cent.). The substance, therefore, is the β -phthalylphenylhydrazide described by Pellizzari (*Gazzetta*, 1886, **16**, 200).

A number of similar experiments, in which portions of the boiling alcoholic sodium ethoxide solution were withdrawn from time to time and precipitated by hydrochloric acid, showed that at first only phthalylphenylhydrazinic acid is obtained, β -phthalylphenylhydrazide slowly making its appearance, and increasing in amount until, after about five to six hours' heating, it alone is present.

Transformation of α - into β -Phthalylphenylhydrazide by Heating with Glycerol.

α -Phthalylphenylhydrazide was heated with about four times its weight of glycerol in an open tube for ten hours to 240° . On cooling, the mass was ground with water and well washed to remove the glycerol. The colourless solid remaining was dissolved in a cold dilute solution of potassium hydroxide, the liquid filtered and acidified with hydrochloric acid, and the white solid separating once crystallised from alcohol.

It melted at 210° , and when mixed with β -phthalylphenylhydr-

azide, prepared from the α -hydrazide and sodium ethoxide, the melting point remained unaltered (Found: C=70.2; H=4.47; N=11.40. Calc.: C=70.59; H=4.20; N=11.77 per cent.). Similar experiments were made in which the time of heating was varied. These showed that the transformation takes place slowly, about 50 per cent. being transformed in from five to six hours.

On similarly heating α -phthalylphenylethylhydrazide with glycerol, no change occurred, the original α -compound crystallising out unaltered from a solution of the product in boiling alcohol, and no other substance separated on evaporation of the filtrate.

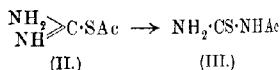
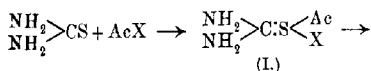
THE QUEEN'S COLLEGE,
OXFORD.

[Received, May 19th, 1920.]

LXXVII.—*The Acylation of Thiocarbamides.*

By AUGUSTUS EDWARD DIXON and JOHN TAYLOR.

It has frequently been observed that the *N*-acylation of thiocarbamide is preceded by the fixation of the acyl radicle to the sulphur atom of the latter (Dixon and Hawthorne, T., 1907, **91**, 127, 145; Dixon and Taylor, *ibid.*, 914; 1908, **93**, 29; 1912, **101**, 2312 *et seq.*; Dixon and Kennedy, this vol., 81), a phenomenon the mechanism of which may be represented by the typical scheme:



On the other hand, in many cases no evidence is yet forthcoming that would justify such a view, the process apparently being accomplished through direct attack of the nitrogen. This, it now appears, is due sometimes (and possibly always) to the instability of the sulphonium salt (I) in the circumstances of its formation.

All such salts are readily dissociable by heat, with the elimination of HX, whence it follows that if a high temperature is essential to reaction, they are not likely to be discoverable in the product. Neither is the ψ -base (II), compounds of this class being always rather unstable. Moreover, a sulphonium salt, although initially formed, may decompose, even in the cold; if so, a substance of type (III) will constitute the actual product, both the others possibly

escaping detection; in either case, *N*-acylation will seem to have occurred directly.

The acetylation of thiocarbamide by means of acetic anhydride is a case in point, heat being employed in the process (Nencki, *Ber.*, 1873, 6, 599). As a matter of fact, reaction occurs spontaneously at the ordinary temperature; the change, however, requires several days for its completion, and at no stage is there a detectable amount of any transition product. Thiocarbamide-acetyl acetate is evidently very unstable: a suspension of thiocarbamide-acetyl iodide in cold acetone, when treated with sodium acetate, rapidly became clear, owing to the formation of sodium iodide, yet from the solution the salt, $\begin{matrix} \text{NH}_2 \\ \text{NH}_2 \end{matrix} > \text{C} : \text{S} < \begin{matrix} \text{COMe} \\ \text{O} \cdot \text{OMe} \end{matrix}$, could not be isolated, the product being merely acetylthiocarbamide.

Nevertheless, that the salt is capable of temporary existence may be inferred from another observation. Thiocarbamide and acetyl picrate, both in glacial acetic acid solution, show no tendency to unite, even after some days' keeping, but when acetic anhydride is added to the mixture, a deposition of thiocarbamide-acetyl picrate soon commences, the reaction within a few hours being complete. The acetyl picrate, therefore, although it fails to unite with the thiocarbamide, reacts with some material produced from the latter by the anhydride, capturing it at once, and thus precluding its normal change into acetylthiocarbamide. Manifestly, this material is either thiocarbamide-acetyl acetate or the corresponding ψ -base (acetyl picrate does not combine with acetylthiocarbamide, and, if it did, the product would not be thiocarbamide-acetyl picrate).

When, instead of acetic acid, dry acetone is used as solvent, the same phenomena occur; but the yellow precipitate, if kept in contact with the liquor, presently redissolves, and later, acetylthiocarbamide is deposited. Thiocarbamide-acetyl picrate, therefore, although producible in contact with acetone, gradually surrenders to it the elements of the conjoined picric acid, whereupon, as usual, the acetyl group of the resultant ψ -base migrates from sulphur to nitrogen. The analogy between the result just mentioned and the foregoing results with (a) thiocarbamide and acetic anhydride, and (b) thiocarbamide-acetyl iodide and sodium acetate, requires no comment.

Observing the production of "diacetylthiocarbamide" from thiocarbamide and acetic anhydride at 130° to be facilitated by the passage of hydrogen chloride into the mixture, E. A. Werner concludes (*T.*, 1916, 109, 1128) that the acid transforms the acetylthiocarbamide into a ψ -configuration, $\text{MeCO} \cdot \text{NH} \cdot \text{C}(\text{NH}) \cdot \text{SH}$,

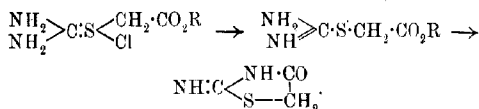
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assumed to be more susceptible of attack by the anhydride. It is far from certain, however, that the hydrogen chloride acts solely on the acetylthiocarbamide, for, at a temperature much lower than 130° , it converts acetic anhydride freely into acetyl chloride, a more active substance than the anhydride. However that may be, the fact is that, in promoting the reaction, acetyl chloride serves just as effectively as hydrogen chloride.

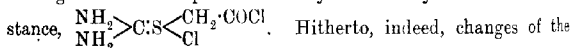
The constitution, $\text{MeCO}\cdot\text{NH}\cdot\text{C}(\text{NH})\cdot\text{S}\cdot\text{COMe}$, proposed by him for "diacetylthiocarbamide" being apparently open to doubt, attempts were made to learn whether the acetylbutyryl derivative (from acetylthiocarbamide and butyryl chloride on the one hand, and from butyrylthiocarbamide and acetyl chloride on the other) could exist in two isomeric forms. The experiments were unsuccessful, as were similar ones in which it was sought to produce acetylbenzoyl derivatives.

isoThiohydantoins.

As regards the behaviour of (say) chloroacetic acid (Rây and Fernandes, T., 1914, 105, 2160) or of its esters (Taylor, this vol., p. 4) towards thiocarbamide, there is no reason to doubt the essential simplicity of the mechanism, represented by the scheme:



Much less simple is the mechanism when (say) chloroacetyl chloride is caused to react with thiocarbamide or with its mono- or di-substitution derivatives, whereby, too, *isothiohydantoins* are produced (Dixon and Taylor, T., 1912, 101, 570). That is, the collocation, $\cdot\text{S}\cdot\text{CH}_2\cdot\text{CO}\cdot$, becomes developed, a result that would be intelligible if the components could yield initially the additive substance,



kind have been represented as occurring on lines more or less consistent with such a view, and it is only of late that, by the authors at least, its inherent difficulties have been recognised.

For example, methylthiocarbamidide with chloroacetyl chloride yields, not $\begin{array}{c} \text{MePhN} \\ \text{PhNH} \end{array} > \text{C} : \text{S} < \begin{array}{c} \text{CH}_2 \cdot \text{COCl} \\ \text{Cl} \end{array}$, but $\begin{array}{c} \text{MePhN} \\ \text{PhNH} \end{array} > \text{C} : \text{S} < \begin{array}{c} \text{CO} \cdot \text{CH}_2\text{Cl} \\ \text{Cl} \end{array}$

(Dixon and Taylor, T., 1912, 101, 570), a result in keeping with the superior activity of the $\cdot\text{COCl}$ fraction of the molecule. With chloroacetyl chloride, too, the speed of reaction is high, just as it is with acid chlorides in general, whereas, unless assisted by heat,

the reaction of a thiocarbamide with a halogenised acid or its ester is relatively very slow. On these grounds, one might expect the formation of isothiohydantoin from thiocarbamide and chloroacetyl chloride (if it takes place on the lines previously supposed) to require at least some hours in the cold; further, by operating in the cold, one might hope, in that case, to isolate the presumable additive salt formulated above.

In practice, when bromoacetyl bromide was added to a solution of thiocarbamide in acetone, isothiohydantoin hydrobromide was precipitated at once, a result tolerably decisive in showing that the fraction, $\cdot\text{CH}_2\text{Br}$, was not the primary agent in the change, but $\cdot\text{COBr}$ instead. If so, and notwithstanding that isothiohydantoin had been generated, it remained now to be shown that the latter

proceeded indirectly, from a compound, $\begin{smallmatrix} \text{NH}_2 \\ \text{NH}_2 \end{smallmatrix} > \text{C} : \text{S} < \begin{smallmatrix} \text{CO} \cdot \text{CH}_2\text{Br} \\ \text{Br} \end{smallmatrix}$. Ultimately, by operation with glacial acetic acid as solvent, that compound was isolated, chloroacetyl bromide in like circumstances furnishing $\begin{smallmatrix} \text{NH}_2 \\ \text{NH}_2 \end{smallmatrix} > \text{C} : \text{S} < \begin{smallmatrix} \text{CO} \cdot \text{CH}_2\text{Cl} \\ \text{Br} \end{smallmatrix}$. By dissolution in water, they

yielded thiocarbamide, hydrobromic acid, and bromo- or chloroacetic acid respectively, but with alkali hydroxide afforded no trace of α -thiolacetic acid, and hence contained no material including the $\cdot\text{S} \cdot \text{CH}_2 \cdot \text{CO} \cdot$ complex. As might have been expected, however, they soon changed when kept in contact with acetone, the respective products being isothiohydantoin hydrobromide and isothiohydantoin hydrochloride.

Of these facts, the explanation, in the light of those acquired in other researches, is now patent. From the additive salt, acetone withdraws the halogen conjoined with sulphur, the product, a β -base, $\text{NH}_2 \cdot \text{C}(\text{NH}) \cdot \text{S} \cdot \text{CO} \cdot \text{CH}_2\text{X}$ ($\text{X} = \text{halogen}$), changing, by the usual migration of the acyl group, into $\text{NH}_2 \cdot \text{CS} \cdot \text{NH} \cdot \text{CO} \cdot \text{CH}_2\text{X}$. No matter how formed, a compound of such type (or, for a matter of that, even of the type $\text{NH}_2 \cdot \text{CS} \cdot \text{NH} \cdot \text{CH}_2 \cdot \text{CH}_2\text{X}$; see Gabriel, *Ber.*, 1889, **22**, 1148) is incapable of existence in ordinary circumstances, changing at once into a cyclic isomeride, the essential nucleus of which is $\text{N} \cdot \text{C} < \begin{smallmatrix} \text{N} \cdot \text{C} \\ \text{S} \cdot \text{C} \end{smallmatrix}$ (Dixon, *T.*, 1897, **71**, 621 *et seq.*).

On the principles now suggested, the explanation of this last change is not far to seek, because, in a molecule such as



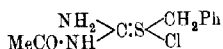
the fractions, $\cdot\text{CH}_2$ and $\cdot\text{X}$, by uniting with the sulphur atom, would yield $\text{NH}_2 \cdot \text{C} < \begin{smallmatrix} \text{NH} \cdot \text{C}() \\ \text{SX} \cdot \text{CH}_2 \end{smallmatrix}$, a formula which the authors take as best expressing the constitution of an isothiohydantoin salt.

Why chloroacetyl chloride when heated with a suitable thiocarbamide yields an isothiohydantoin is now clear, for the sulphonium salt, initially formed, since it loses haloid acid by mere contact with acetone, must very readily be dissociable by heat. How pyridine facilitates acylation in the cold (Dixon and Taylor, T., 1912, **101**, 2518) is equally clear: it removes from the sulphonium salt the elements of an acid, without hydrolysing the resultant acylated ψ -base.

ψ -Thiocarbamides.

From methyl- ψ -thiocarbamide and benzoyl chloride, in the presence of alkali hydroxide, Johnson and Jamieson (*Amer. Chem. J.*, 1906, **35**, 297) obtained the compound $(\text{PhCO})_2\text{N}\cdot\text{C}(\text{NH})\cdot\text{SMe}$. On the other hand, in the absence of an alkali, benzyl- ψ -thiocarbamide, even with a large excess of acetyl chloride, yields only the additive compound, $\text{CSN}_2\text{H}_3\cdot\text{Cl}_2\text{Ph}\cdot\text{MeCOCl}$, from which, on the withdrawal of hydrogen chloride, there results a monoacylated derivative of the ψ -thiocarbamide. Whether the additive com-

pound is $\begin{array}{c} \text{NH}_2 \\ \text{NH} \end{array} \gg \text{C} \cdot \text{S} \cdot \text{Cl} \begin{array}{c} \text{CH}_2\text{Ph} \\ \text{COMe} \end{array}$ or (more likely)



matters little: in either case, the sulphur atom, by the absorption of a single molecule of the acid chloride, has become fully charged, and until a condition is established favourable to the elimination of hydrogen chloride, further acetylation is barred.

A case not here touched on, except incidentally, is the behaviour of acylating agents with thiocarbamides containing a well-marked electronegative group. In this connexion, owing to the difficulty with which the substances combine spontaneously (Dixon and Hawthorne, T., 1907, **91**, 141), little is yet known of the mechanism.

Thiocarbamides containing an NH_2 -substituent (thiosemicarbazides) combine directly with acetyl chloride, yielding well-marked salts, from which, on the withdrawal of hydrogen chloride, *N*-acetyl derivatives are produced (McKee, T., 1915, **107**, 1133). In these, not only the acetyl radicle, but also a phenyl group, can migrate from one point to another within the molecule.

EXPERIMENTAL.

I. Thiocarbamide-acetyl chloride was dissolved in cold pyridine, the solution when acidified with dilute acetic acid

depositing acetylthiocarbamide. Heat, therefore, is not essential to the transformation, $\text{NH}_2\text{C}(=\text{NH})\text{S}\cdot\text{COMe} \rightarrow \text{NH}_2\text{CS}\cdot\text{NH}\cdot\text{COMe}$.

By boiling for an hour with acetone, the same change is effected. Aniline behaves differently, heat being evolved, with the production of acetanilide, but ready-formed acetylthiocarbamide is practically unaffected by aniline, even on heating.

II. Finely sifted thiocarbamide was kept at the ordinary temperature in contact with excess of acetic anhydride. Gradually, the powder disappeared, its place being taken completely, after the lapse of a week, by large, transparent, rhombic prisms. Neither they nor the liquor in which they were formed yielded at any time a precipitate with aqueous picric acid; hence, neither thiocarbamide-acetyl acetate nor acetyl- ψ -thiocarbamide was present in quantity. The crystals consisted of almost pure acetylthiocarbamide (yield, 52 per cent. of the theoretical), and from the liquor, on concentration, a further amount of slightly impure material was obtained.

Acetylthiocarbamide with dilute acetic acid and sodium nitrite yields in one minute a scarcely perceptible trace of thiocyanic acid; in like circumstances, thiocarbamide (compare Werner, T., 1912, 101, 2183) gives a well-marked reaction in less than thirty seconds.

III. From thiocarbamide dissolved in acetone and acetyl iodide, crystals of the additive salt, $\text{NH}_2\text{C}(=\text{NH})\text{S}\cdot\text{COMe}\cdot\text{I}$, were deposited.

It melted and decomposed at about 106° , and yielded a *picrate*, but was soon resolved by cold water into thiocarbamide, acetic acid, and hydriodic acid (total acid found = 13/14ths of that calculated).

A suspension of the salt in dry acetone, when treated with one molecular proportion of dry sodium acetate, rapidly became clear, sodium iodide passing into solution (sodium acetate is practically insoluble in acetone). The solution, which gave no precipitate with aqueous picric acid, and hence no longer contained thiocarbamide-acetyl iodide, was concentrated at a low temperature to expel most of the acetone; it now had the pungent odour of acetic acid, and presently yielded crystals of acetylthiocarbamide.

When the experiment was performed with thiocarbamide-acetyl chloride, instead of the iodide, scarcely any sign of interaction was perceptible in the cold. On heating, acetylthiocarbamide was produced, together with sodium chloride, a result not necessarily due, however, to reaction between the first-named material and the sodium acetate (see I).

IV. From a solution of thiocarbamide in acetone, on treatment with isobutyryl chloride, the additive salt, $\text{NH}_2\text{C}(\text{NH}_2)\text{S}\text{C}(\text{O})\text{C}_2\text{H}_5$, was precipitated in flattened, lustrous needles melting, with effervescence, at 115—117°, and yielding with aqueous picric acid a bright yellow *picrate*, hydrolysed by warming with water (Found: Cl=19.25. $\text{C}_6\text{H}_{11}\text{ON}_2\text{ClS}$ requires Cl=19.5 per cent.). By heating at 120—130° until effervescence ceased, and recrystallising the product from water, isobutyrylthiocarbamide was obtained in pearly leaflets melting at 111—112° (Found: S=21.92. Calc.: S=21.91 per cent.).

An attempt, by heating the latter with acetyl chloride and glacial acetic acid, to produce a derivative containing both acetyl and isobutyryl was unsuccessful; neither did acetylthiocarbamide when heated with isobutyryl chloride yield the expected diacyl compound.

V. Acetylthiocarbamide when heated under reflux with benzoyl chloride in the presence of glacial acetic acid in a bath at 130—150° gave a solid, from which chloroform extracted a crystalline, yellow substance melting at 105°, and consisting, apparently of the acetylbenzoyl derivative (Found: S=14.4. Calc.: S=14.4 per cent.). From benzoylthiocarbamide, however, similarly heated with acetyl chloride and acetic anhydride, nothing was obtained except benzoic acid and diacetylthiocarbamide.

VI. Into acetic anhydride at 115° excess of hydrogen chloride was passed, the solution, when distilled, yielding acetyl chloride in quantity. When the experiment was repeated, at 130°, with thiocarbamide in solution, the phenomena described by Werner (T. 1916, 109, 1128) were verified, the product being a diacetyl derivative.

VII. Acetyl chloride was substituted for hydrogen chloride in an experiment similar to the last, the phenomena being visually the same as before, and from the solution, after it had been concentrated in a vacuum over sodium hydroxide, the same diacetyl compound was obtained. A like result followed when acetyl chloride was heated for some time with a solution of acetylthiocarbamide in glacial acetic acid under reflux.

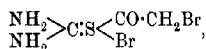
VIII. A solution of picric acid in acetic anhydride, when kept for a few hours in contact with finely powdered thiocarbamide, transformed the latter completely into thiocarbamide-acetyl picrate melting at 120° (Found: S=9.2. Calc.: S=9.21 per cent.).

Ready-formed acetyl picrate and thiocarbamide, each dissolved in glacial acetic acid, showed, after two days' keeping, no sign of

interaction. When acetic anhydride was added to the mixture, crystals of thiocarbamide-acetyl picrate began to separate in the course of an hour or so, and, after about seven hours, were collected, the filtrate remaining permanently clear.

IX. Bromoacetyl bromide, when added to a cold solution of thiocarbamide in acetone, yielded a sandy, white powder readily soluble in water, and giving all the reactions of isothiohydantoin hydrobromide (Found: S=16.2; HBr=41.4. Calc.: S=16.24; HBr=41.11 per cent.).

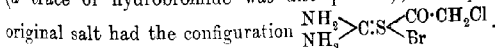
X. The preceding experiment being repeated with glacial acetic acid as solvent, white needles of the additive compound,



were deposited, highly deliquescent and readily soluble in water. The very acid aqueous solution yielded with picric acid only a slight precipitate, but contained hydrobromic and bromoacetic acids, together with thiocarbamide. It gave no precipitate when neutralised, and, after short boiling with dilute alkali hydroxide, it did not give Andreasch's reaction (*Ber.*, 1879, 12, 1385) for α -thioacetic acid, and hence contained no detectable trace of isothiohydantoin (Found: S=12.2. $\text{C}_3\text{H}_6\text{ON}_2\text{Br}_2\text{S}$ requires S=11.51 per cent. Total acid=39/40ths of that calculated).

The salt, when kept for an hour in contact with dry acetone, changed little in appearance, except that it became granular; the residual solid, now no longer deliquescent, gave all the usual reactions of isothiohydantoin hydrobromide, including the formation of a *picrate*, not hydrolysed by heating with water, but reappearing when its solution was cooled.

XI. When the last experiment was repeated, but with chloroacetyl bromide, a similar additive compound was obtained in rosettes of white prisms, decomposing at 110–112° (Found: Br+Cl=49.5. $\text{C}_3\text{H}_6\text{ON}_2\text{ClBrS}$ requires Br+Cl=49.46 per cent.). By dissolution in water, it gave thiocarbamide, hydrobromic acid, and chloroacetic acid, but not instantaneously, for the solution, if mixed at once with picric acid, yielded a bright yellow *picrate*, hydrolysed by gently heating with water. On contact with dry acetone, the substance lost the elements of hydrogen bromide, the residual solid consisting mainly of isothiohydantoin hydrochloride (a trace of hydrobromide was also present); consequently, the original salt had the configuration



XII. To benzyl- ψ -thiocarbamide in acetone a large excess of acetyl chloride was added, the white precipitate at first formed dissolving as the addition was continued. On cooling, rosettes of

slender needles were deposited, melting and decomposing at 140—142°, and having the properties to be expected of an additive salt. Notwithstanding that a great excess of the chloride had been used, a single molecular proportion alone reacted, the product being $\text{CSN}_2\text{H}_3\cdot\text{CH}_2\text{Ph}\cdot\text{MeCOCl}$ (Found: $\text{Cl}=14\cdot7$. $\text{C}_{10}\text{H}_{13}\text{ON}_2\text{ClS}$ requires $\text{Cl}=14\cdot52$ per cent.), and from it the monoacetyl base was liberated by means of calcium carbonate (Found: $\text{S}=15\cdot6$. $\text{C}_{10}\text{H}_{12}\text{ON}_2\text{S}$ requires $\text{S}=15\cdot38$ per cent.). It melted at 132°; but the same base, prepared from acetylthiocarbamide and benzyl chloride, shrank at 125° and melted at 128° (Found: $\text{S}=15\cdot5$).

The substance, presumably $\text{NH}_2\cdot\text{C}(\text{N}\cdot\text{COMe})\cdot\text{S}\cdot\text{CH}_2\text{Ph}$, was obtained in such poor yield (sometimes none at all) as to defeat projected experiments on its further possible combination with acetyl chloride.

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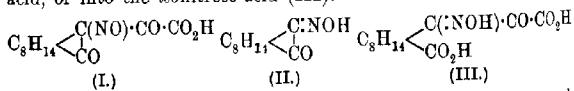
[Received, May 20th, 1920.]

LXXVIII.—*A New Series of Nitrogenous Compounds obtained from Camphoroxalic Acid.*

By PERCY CHORLEY and ARTHUR LAPWORTH.

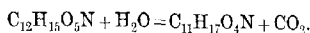
WHEN nitrous acid reacts with compounds containing the group $\cdot\text{CO}\cdot\text{CHR}\cdot\text{CO}\cdot$, the nitroso-compounds, $\cdot\text{CO}\cdot\text{CR}(\text{NO})\cdot\text{CO}\cdot$, which are doubtless the initial products in all instances, tend to absorb the elements of water (or alcohol), with simultaneous severance of a "bond" between two of the carbon atoms in the second structure above depicted, yielding $\cdot\text{CO}_2\text{H}$ (or $\cdot\text{CO}_2\text{Et}$) and $\cdot\text{CR}(\text{NOH})\cdot\text{CO}\cdot$.

In the course of experiments which were instituted for the purpose of simplifying the methods at present available for converting ketones into their *isonitroso*-derivatives, the action of nitrous acid on camphoroxalic acid was studied. It was anticipated that the nitroso-compound (I) of this substance would show complete analogy to the nitroso-derivatives of substituted malonic and acetoacetic acids, and become converted, with absorption of the elements of water, either into *isonitrosocamphor* (II) and oxalic acid, or into the *isonitroso*-acid (III).



A transient blue colour, doubtless that of the nitroso-compound

(I), is observed when nitrous acid acts on camphoroxalic acid in aqueous solution. A small quantity of isonitrosocamphor (II) is formed, but the main quantity of the nitroso-compound decomposes, with the elimination of carbon dioxide and the formation of a crystalline acid (A_1), $C_{11}H_{17}O_4N$, apparently in accordance with the equation



The properties of the new acid are very difficult to reconcile with any quite straightforward assumptions as to its structure. It evinces remarkable stability towards both acids and alkalis; hot concentrated hydrochloric acid has no appreciable effect on it; boiling 50 per cent. aqueous potassium hydroxide, after prolonged contact, does not cause elimination of ammonia or hydroxylamine, but merely converts it into an isomeric acid (A_2), the properties of which so closely resemble those of the original compound as to leave little or no doubt that the isomerism is steric in character.

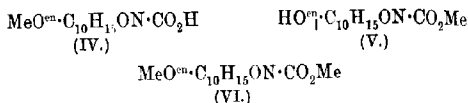
The most important properties of the acid (A_1) are the following:

- (1) It is a monobasic acid with distinct amphoteric characters.
- (2) It reacts very readily with phosphorus pentachloride, and the product is at once converted by water into the original acid.
- (3) It yields camphoric acid when oxidised.
- (4) It is devoid of ketonic or aldehydic properties.
- (5) It is easily reduced by ferrous hydroxide in the presence of alkalis, although many of the ordinary reducing agents are without appreciable effect on it.
- (6) It gives an intense red coloration with aqueous ferric chloride.

The behaviour of the acid (A_1) on methylation is very significant. When methylated with methyl sulphate and alkali, it is converted into (a) a monomethyl "derivative" which is capable of expelling carbon dioxide from aqueous sodium carbonate, but gives no coloration with ferric chloride, and (b) a dimethyl "derivative" which is devoid of all acid properties, gives no coloration with ferric chloride.

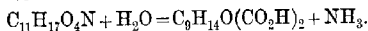
The methyl groups in the dimethyl "derivative" are evidently both attached to oxygen, and not to nitrogen, for when this compound is hydrolysed by means of alkalis, the whole of its nitrogen is liberated in the form of ammonia, and no trace of methylamine can be detected. The coloration with ferric chloride which the original acid and its monomethyl "derivative" afford, indicates very clearly that in these two compounds there is present a grouping of the enol type, that is, $\dot{C}:C(OH)\cdot$ or $\cdot N:C(OH)\cdot$. On the other hand, the pronounced acidity of the acid and of its monomethyl "derivative" points to the presence in their molecules of

the free carboxyl group, a conclusion with which the behaviour of the acid towards phosphorus pentachloride is in entire agreement. The following formulæ serve to indicate the relation between the monomethyl "derivative" (IV), the true monomethyl ester, hitherto not isolated (V), and the dimethyl "derivative" (VI). The sign O^{en} is used to emphasise the conclusion that the oxygen atom is associated with doubly-bound carbon (enol type of structure).

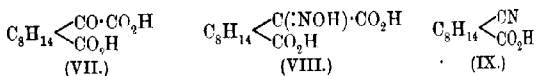


The ease with which the acid (A_1) is reduced by means of ferrous hydroxide affords evidence that the nitrogen atom is directly attached to oxygen, but as the reactions of the compounds exclude the occurrence of the groups $>\text{C}\cdot\text{NOH}$ and $\cdot\text{C}\cdot\text{NH}\cdot\text{OH}$, it must be inferred that the complex $>\text{N}\cdot\text{O}\cdot$ is present as part of a ring. The ready response to alkaline ferrous hydroxide shown by certain isooxazolones, which also have this structural peculiarity, has previously been noticed (T., 1907, **91**, 1919).

Whilst the original acid (A_1) is remarkably stable towards alkalis, the dimethyl derivative is readily hydrolysed by them, with evolution of ammonia and formation of a dibasic acid, $\text{C}_9\text{H}_{14}\text{O}(\text{CO}_2\text{H})_2$, in accordance with the equation:



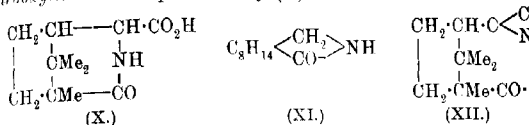
This substance has all the characters of an α -ketonic acid, and is readily oxidised by lead dioxide or manganese dioxide in aqueous solution. Its oxime when heated loses water and carbon dioxide, and is converted into α -camphornitrilic acid (IX), which observation decides the structure of the ketonic acid as (VII), and that of the oxime as (VIII).



Additional light was thrown on the structure of the acid (A_1) by a study of the product which is obtained on reducing it with alkaline ferrous hydroxide. This product is a monobasic acid, $\text{C}_{11}\text{H}_{17}\text{O}_3\text{N}$, and is formed by the simple withdrawal of one atomic proportion of oxygen from the molecule of the parent acid. The new substance is extraordinarily stable towards powerful acids and alkaline hydrolytic agents, but its silver salt decomposes fairly

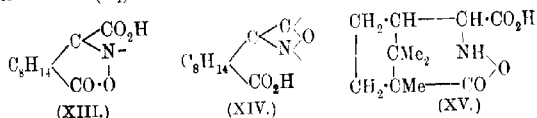
regularly in a stream of carbon dioxide, and the distillate consists almost wholly of α -camphidone (XI).

The properties of the monobasic acid are readily explained on the assumption that it is the monocarboxylic acid of α -camphidone (XI), and consideration of the relation of the present series of compounds to nitrosocamphoroxalic acid (I) and to α -ketohomocamphoric acid (VII) shows that the structure of the *camphidone-carboxylic acid* is represented by (X).



It has been already remarked that in the formation of the acid (A_1) from camphoroxalic acid, the nitroso compound (I) represents an intermediate step. This, taken in conjunction with the conversion of A_1 into camphidonecarboxylic acid (X) on the one hand, and into α -ketohomocamphoric acid (VII) on the other, leaves no reasonable doubt that the acid (A_1) and its derivatives contain the structure (XII).

In order to satisfy the further conditions: (1) that the molecule includes the structure $\dot{\text{N}}\cdot\text{O}$ as part of a ring, and (2) that one carboxyl group is present, one of the two following skeleton structures must be selected as the framework of any structural formula for the acid (A_1):

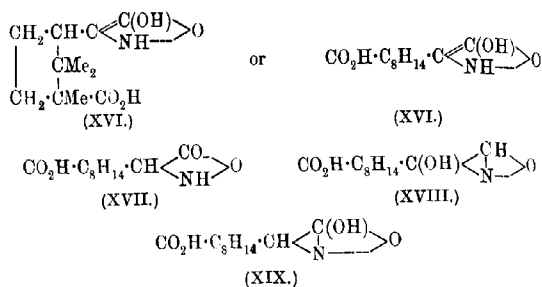


The only possible structural formula for a compound, $\text{C}_{11}\text{H}_{17}\text{O}_4\text{N}$, based on (XIII) is (XV).

This is, however, wholly incompatible with the behaviour of the substance on methylation, as the lactonic carbonyl group would be attached to a quaternary carbon atom, and such a structure cannot be considered capable of existence in an enolic form without doing violence to all accepted canons. Formation of a dimethyl ester would necessitate the absorption of the elements of water, and this does not occur.

The authors, after very long consideration, have been forced to adopt (XIV) as the basis of a formula for the ultimate product obtained by the action of nitrous acid on camphoroxalic acid. On this basis, several "tautomeric" forms are possible for the acids

A_1 and A_2 , and these, without introducing various other possibilities suggested by internal-salt formation, are as follows:



Of these, probably (XVI) and its ketonic form (XVII) are much to be preferred, as (XVI) is the only one which contains the true enol grouping $\cdot\text{C(OH)}:\dot{\text{C}}\cdot$, towards which the properties of the acids A_1 and A_2 significantly point. On the other hand, (XVIII) and (XIX) cannot yet finally be excluded, and they recall the structures which have long been adopted as the most satisfactory ones for anthranil, anthroxamic acid, and especially for the "oxy-anthranil" or benzisoxazolone of Bamberger and Pyman (*Ber.*, 1909, **42**, 2299).

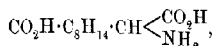
In each of the above formulæ there is present a four-membered heterocyclic nucleus never previously identified in any compound, and until further instances of the structure come to light, the question of a suitable nomenclature for the present series of substances may be deferred.

It is worthy of note that the formation from the nitroso-compound (I) of a substance having any of the structures (XVI), (XVII), (XVIII), or (XIX) is associated with an engagement between the nitroso-group and the ketonic carbon atom in the complex, $\cdot\text{CO}\cdot\text{CO}_2\text{H}$. This renders it easy to understand what is otherwise incomprehensible, namely, why carbon dioxide should be eliminated during the formation of the acid (A_1), for the relations of the carbon atom to which the carbonyl group is attached are fundamentally altered by such an engagement. Such a consideration lends considerable weight to the more formal reasons which independently led the authors to reject (XV) and all other formulæ than those containing the four-membered rings.

The isomerism of the acids A_1 and A_2 is probably not such as exists, for example, between any two of the four alternative formulæ above given. It is more likely that both acids are expressed by the same plane formula, and differ only in the spacial

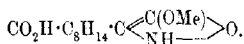
relations of the atoms and groups about the four-membered ring. It is not impossible that the stereochemistry of the nitrogen atom is here involved.

The reduction of the acid (A_4) to α -camphidonecarboxylic acid by means of alkaline ferrous hydroxide is understood readily enough with the aid of formula (XVI) in association with the fact that this agent converts the group $>N\cdot O\cdot$, even when present as part of a ring, into $>NH$, if necessary with ring scission. Thus (XVI) becomes reduced to

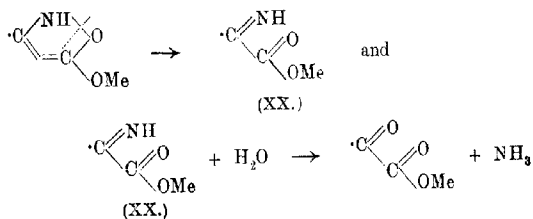


which would at once, on acidification, undergo conversion into its lactam, and the latter is nothing else than the α -camphidonecarboxylic acid (X) in question.

Adopting (XVI) for the acid A_1 , the structure of the acid methyl "derivative" of this becomes



The mechanism by which this substance yields ammonia, methyl alcohol, and α -ketohomocamphoric acid on treatment with alkali is somewhat obscure, but, as it involves the intramolecular reduction of an $>N\cdot O\cdot$ group, it is perhaps not distantly related to the "Beckmann change" of oximes. A simple rearrangement of the bonds in the four-membered ring of the above structure corresponds with such a reduction, and furnishes a new structure which obviously represents the imino-derivative (XX) of α -ketohomocamphoric methyl ester (XXI), which on hydrolysis would, of course, yield exactly the products actually observed.

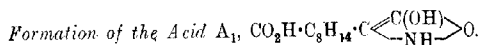


EXPERIMENTAL.

Ethyl camphoroxalate was prepared by the action of sodium on a mixture of ethyl oxalate and camphor (compare Tingle, *Amer. Chem. J.*, 1897, **19**, 393), but in working up the product considerable improvements were effected by subjecting the crude

material to the action of a current of steam for about fifteen minutes. The latter treatment removes unaltered camphor with other volatile impurities, and the residual oil, collected and exposed over sulphuric acid in a vacuum for some hours, crystallises, if subsequently cooled in a freezing mixture, and then merely requires draining on porous earthenware before crystallisation from light petroleum.

To obtain camphoroxalic acid, the crude product, after treatment with steam, can with advantage be hydrolysed by leaving it in contact with 10 per cent. cold aqueous potassium hydroxide for three days. Subsequent addition of dilute sulphuric acid causes precipitation of camphoroxalic acid in a state sufficiently pure for most purposes.



Camphoroxalic acid (20 grams), dissolved in a 10 per cent. solution of aqueous sodium hydroxide (40 c.c.), is mixed with a 10 per cent. solution (63.8 c.c.) of sodium nitrite. Ten per cent. hydrochloric acid (100 c.c.) is then added very slowly below the surface of the liquid, when at first each small addition produces a white precipitate, which almost at once dissolves, forming an intensely green solution. This colour is not very fugitive at 10°, but at the ordinary temperature rapidly changes to yellow; it is not in any way due to free nitrous acid, as the solution does not react with starch-potassium iodide paper; the phenomena rather indicate the presence of a true nitroso-compound.

The continued addition of hydrochloric acid, which should occupy in all about ninety minutes, ultimately leads to the evolution of carbon dioxide and the separation of a brown oil, which contains free camphor, camphorquinone, and camphoroxalic acid. The aqueous liquor is separated from the oil and evaporated under diminished pressure nearly to dryness, during which process an appreciable quantity of camphorquinone at first passes over. The concentrated residue deposits a white solid when cool; the latter is removed, drained, extracted with ethyl acetate, and the extract filtered and cooled. A mass of white needles is then obtained, the quantity of which can be increased by further similar treatment of the filtrate, and the total yield approaches 77 per cent. of that theoretically possible.

The new substance is best purified by crystallisation from ethyl acetate, from which it reappears as a felted mass of needles. It dissolves freely in water, forming a strongly acid solution, and it is freely soluble also in alcohol, acetone, ethyl acetate, or chloro-

form; it is not freely dissolved by ether, and is insoluble in benzene or light petroleum.

Hydrochloric acid greatly increases the solubility of the compound, which therefore displays a basic as well as an acid character.

The crystals from ethyl acetate contain solvent of crystallisation, which, however, is rapidly lost on exposure to the atmosphere. A specimen left until constant in weight was analysed (Found: C=58.2; H=7.6; N=5.9. M.W.=230. $C_{11}H_{17}O_4N$ requires C=58.2; H=7.5; N=6.2 per cent. M.W.=227).

0.1605 Gram required 28.3 c.c. of 0.0248 *N*-NaOH for neutralisation, using phenolphthalein; equivalent=229. A monobasic acid, $C_{11}H_{17}O_4N$, has the equivalent 227.

0.6388 Gram dissolved and made up to 10 c.c. with absolute alcohol at 17° gave α_D 0.39° in a 1-dcm. tube, whence $[\alpha]_D^{25}$ 6.10°.

The pure compound melts at 160°, simultaneously evolving carbon dioxide and leaving a residue devoid of acid characters, but still more decidedly basic than the original substance. It is remarkably stable towards acids, and no change could be detected in it after prolonged boiling with saturated aqueous hydrochloric acid or after heating for six hours on the water-bath with concentrated sulphuric acid or aqueous hydrobromic acid. Hydrogen peroxide had no effect on it, but nitric acid oxidised it to camphoric acid with great facility. It is vigorously attacked by phosphorus pentachloride in dry ether, hydrogen chloride being copiously evolved; but the product, on treatment with ice-water, is at once converted into the original acid, and this suggests that the product in question is the normal carboxylic chloride.

The acid in aqueous solution gives an intense violet-red coloration with ferric chloride. It does not reduce Fehling's solution even after prolonged boiling with hydrochloric acid. No oxime, semicarbazone, or hydrazone could be prepared from it. Under certain conditions it reacts, in the presence of alkali, with toluene-sulphonyl chloride, yielding an unstable, non-acidic oil, which dissolves in dilute hydrochloric acid; the true nature of this oil and the precise conditions necessary for its formation have not been determined.

The dilute solution of the sodium salt gives no precipitates with salts of silver, mercury, or barium, but with copper acetate it yields a bright green precipitate, which is soluble both in alcohol and chloroform; with lead acetate, a white salt is deposited unless the dilution is excessive.

Formation of the Isomeric Acid A₂, $\text{CO}_2\text{H}\cdot\text{C}_8\text{H}_{14}\cdot\text{C}\begin{smallmatrix} \text{C(OH)} \\ \text{NH} \end{smallmatrix}\text{O}$.

This is formed when the original acid (A₁) (10 grams) is boiled for twenty-four hours with a 50 per cent. solution of potassium hydroxide (100 c.c.). It is isolated by acidifying with hydrochloric acid and extracting with ether, and crystallises from ethyl acetate in colourless prisms, which are free from solvent of crystallisation (Found: C=57.9; H=7.6; N=6.2. $\text{C}_{11}\text{H}_{17}\text{O}_4\text{N}$ requires C=58.2; H=7.5; N=6.2 per cent.).

0.1738 Gram required 61.5 c.c. of 0.01240 *N*-NaOH for neutralisation, using phenolphthalein; equivalent=227. Calc., 228.

0.3809 Gram, dissolved and made up to 10 c.c. with absolute alcohol, gave α_D 0.99° at 17° in a 1-dcm. tube, whence $[\alpha]_D^{25}$ 25.99°.

The substance melts and decomposes at 205°, evolving carbon dioxide and leaving a basic residue; it closely resembles the isomeride in all essential chemical characters and in its behaviour towards solvents. In aqueous or alcoholic solution, it gives intense violet-red colorations with ferric chloride, and when dissolved in aqueous sodium hydrogen carbonate it instantly decolorises potassium permanganate. It is not appreciably hydrolysed by either hot aqueous alkalis or acids. The salts are freely soluble in water, with the exception of that of lead.

The acid behaves towards methyl sulphate and alkali in much the same manner as does the isomeride; no serious attempt has been made to purify the product, which is usually oily, but it was observed that it readily evolved ammonia when boiled with 50 per cent. potassium hydroxide. The similar behaviour of the isomeride in these circumstances is described later.

Thermal Decomposition of the Acid A₁.

When the original carboxylic acid is heated above its melting point, it evolves carbon dioxide and leaves a resinous mass. The product obtained by heating 90 grams of the acid at 160–170° for forty-five minutes dissolved completely in concentrated hydrochloric acid, but the solution, when diluted, deposited a considerable amount of tarry matter easily separated by filtration; the filtrate, rendered strongly alkaline with sodium hydroxide, yielded to ether 1.4 grams of a yellow base, freely soluble in the common oxygen-containing solvents, but sparingly so in benzene or petroleum. The base was obtained in fern-like plates, melting and decomposing at 232°, by extraction with boiling petroleum (b. p. 100–120°).

Analyses and molecular-weight determinations of different pre-

parations of the base gave numbers indicating the presence of a compound having the formula $C_{10}H_{17}O_2N$, but contaminated with 10–20 per cent. of another, $C_{10}H_{17}ON$ or $C_{10}H_{15}ON$, this suggesting that partial reduction or dehydration accompanies the elimination of carbon dioxide from the carboxylic acid; all attempts to separate the constituents of the mixture by fractional crystallisation before or after conversion into picrates were fruitless. The mixture gives no coloration with ferric chloride, and in many respects resembles α -camphidone, although the presence of the latter seemed improbable, as no characteristic picrate could be prepared from the material.

Methylation of the Acid A_1 .

(a) *With the Silver Salt and Methyl Iodide.*—The silver salt was prepared by neutralising the aqueous solution of the acid with silver carbonate, evaporating to dryness, and heating the residue cautiously. It was then heated with methyl iodide in anhydrous ether for two hours. The filtered ethereal solution, evaporated to dryness, gave an oil, which, when washed with aqueous sodium hydrogen carbonate, was converted into a white solid, insoluble in water. This melted at about 230° , had no acidic properties, but gave an intense red coloration with ferric chloride in alcoholic solution. When boiled with water, it slowly dissolved, forming a solution which responded to the same tests as did the original carboxylic acid. The substance did not, however, respond to the tests for a methyl ester, and its nature remains uncertain, although analysis showed that the elements of carbon dioxide had been lost; it may be identical with one of the products obtained on heating the acid A_1 .

(b) *With Alkali and Methyl Sulphate.*—The acid (18.5 grams) was dissolved in methyl alcohol (100 c.c.) containing methyl sulphate (24 grams). To this was then added gradually methyl alcohol (200 c.c.) containing potassium hydroxide (20 grams), and the whole allowed to remain during the night. The alcohol was then removed by evaporation and the residue dissolved in water, the resulting solution being extracted with ether. From the latter about 6 grams of a basic oil were obtained, whilst the residual aqueous liquor, when acidified with hydrochloric acid and again extracted with ether, yielded about 13 grams of a colourless acid.

The Monomethyl "Derivative," $\text{CO}_2\text{H}\cdot\text{C}_8\text{H}_{14}\cdot\text{C}\begin{smallmatrix} \text{C(OMe)} \\ \text{---NH---} \end{smallmatrix} \text{O}$.

The foregoing colourless acid was purified by crystallisation from acetone (Found: C=59.4; H=7.9; N=6.0. $\text{C}_{12}\text{H}_{19}\text{O}_4\text{N}$ requires C=59.7; H=7.9; N=5.8 per cent.).

The equivalent, determined by titration with sodium hydroxide, using phenolphthalein, was 232; Calc., 241. The substance separates from acetone in large, colourless octahedra, which melt and decompose slightly at 172° . It dissolves freely in alcohol, water, acetone, or ethyl acetate, less readily in ether or benzene, and is insoluble in cold light petroleum. Its aqueous solution gives no coloration with ferric chloride, but instantly decolorises permanganate and bromine water. When boiled with concentrated aqueous alkalis, it is decomposed, as described later.

If the silver salt of this acid is distilled in a vacuum, carbon dioxide is eliminated, and a basic solid distils. This solid is not homogeneous, but when fractionated by recrystallisation from petroleum (b. p. $60\text{--}70^\circ$) yields a crystalline material closely resembling impure α -camphidone; on recrystallisation of the picrate, a salt was isolated which had the same form as the picrate of α -camphidone, but the melting point was much too low, and the identity of the above solid remains somewhat doubtful.

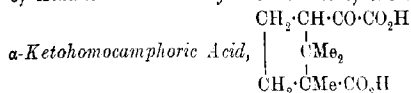
The Dimethyl "Derivative" (Methyl Ester of the Monomethyl "Derivative"), $\text{CO}_2\text{Me}\cdot\text{C}_8\text{H}_{14}\cdot\text{C}\begin{smallmatrix} \text{C(OMe)} \\ \text{---NH---} \end{smallmatrix} \text{O}$.

The basic substance obtained during the methylation of the hydroxycarboxylic acid was purified by crystallisation from dilute alcohol (Found: C=60.9; H=7.7. $\text{C}_{13}\text{H}_{21}\text{O}_4\text{N}$ requires C=61.2; H=8.2 per cent.).

This ester, although somewhat sparingly soluble in cold water, readily forms supersaturated solutions in it, and from these, on nucleation, it separates in slender needles, which in the course of a few days change into rhombic prisms melting at 115° . It dissolves freely in hot water, and also in ether, alcohol, acetone, or benzene, but only sparingly in petroleum.

In virtue of its basic character, the ester is freely soluble in weak or concentrated hydrochloric acid, and is reprecipitated on addition of alkali.

Action of Alkalis on the Methyl Derivatives of the Acid A₁.



Both the monomethyl derivative of the acid A₁ and the dimethyl derivative, or methoxy-ester, are decomposed by boiling 50 per cent. potassium hydroxide. In both instances, ammonia, without any detectable trace of methylamine, is evolved.

The decomposition is best carried out with the monomethyl derivative; here, in the initial stage of the reaction, the crystals change to an opaque mass, probably due to deposition of potassium salt, and this is soon converted into an oil. The oil quickly dissolves, and a sudden evolution of ammonia takes place. Action ceases after about ten minutes' boiling, when the solution may be cooled, acidified with hydrochloric acid, and extracted with ether, which removes a viscid, strongly acid oil. It was found exceedingly difficult to purify this product; at the end of some weeks' exposure it sets to a pulp, which may be triturated with concentrated hydrochloric acid, allowed to remain with it for some hours, and then transferred to porous earthenware. The white solid which is finally obtained in this manner can be further purified by dissolving it in the minimum quantity of anhydrous formic acid, and then adding concentrated hydrochloric acid until a permanent milkiness results. After some hours, a quantity of the substance is deposited in white needles, which can be separated and exposed over paraffin wax and potassium hydroxide in a vacuum for several days (Found: C=56.2, 58.4; H=6.9, 7.0. C₁₁H₁₆O₅ requires C=57.9; H=7.0 per cent.).

Samples titrated with alkali in the presence of phenolphthalein gave numbers for the equivalent somewhat wide of the mark, but showed the acid to be dibasic.

In spite of the unsatisfactory analytical data, there can be no doubt that the formula given represents the composition of the pure substance. The latter is excessively hygroscopic, but is nevertheless not readily soluble in water. It dissolves sparingly in benzene and still less readily in petroleum, but is freely soluble in alcohol, ether, acetone, or ethyl acetate; it does not appear to crystallise from any of these solvents, but separates as an oil. The acid in aqueous solution gives with ferric chloride a blue coloration, which disappears slowly in the cold and rapidly near 100°.

The *lead* salt is but slightly soluble in water. The *silver* salt is

sparingly soluble in cold water, but dissolves somewhat freely in hot; it is not rapidly decomposed on exposure to light.

When α -ketohomocamphoric acid is heated, it melts at 135–139° with slight decomposition; at 170°, the decomposition occurs rapidly, carbon monoxide and water being evolved, and a white, crystalline sublimate formed. This sublimate was purified by distillation in a current of steam and recrystallised from petroleum (Found: C=66.2; H=7.7. $C_{10}H_{14}O_3$ requires C=66.0; H=7.7 per cent.).

The product melted at 218–219°, and its identity with camphoric anhydride was completely established by the usual methods.

α -Ketohomocamphoric acid reduces boiling dilute copper sulphate solution; lead or manganese dioxides added to its warm aqueous solution instantly cause evolution of carbon dioxide with effervescence.

The *phenylhydrazone*, $CO_2H \cdot C_8H_{14} \cdot C(CO_2H) : N_2HPh, H_2O$, was prepared by mixing the acid in about 1 per cent. aqueous solution with phenylhydrazine acetate; the solid which separated was crystallised from dilute methyl alcohol (Found: C=61.2; H=7.6; N=8.4. $C_{17}H_{22}O_4N_2 \cdot H_2O$ requires C=60.8; H=7.1; N=8.3 per cent.).

The compound crystallises in needles and melts at 184°, with slight decomposition; it dissolves in aqueous sodium hydrogen carbonate, displacing carbon dioxide.

α -isNitrosohomocamphoric Acid, $CO_2H \cdot C_8H_{14} \cdot C(:NOH) \cdot CO_2H$.

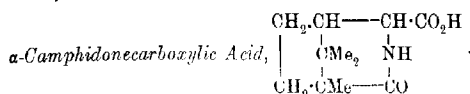
The ketonic acid (1 gram) was heated for an hour on the water-bath with a solution of free hydroxylamine (about 1 gram) in absolute alcohol. The oil obtained by subsequently removing the alcohol did not crystallise, and had to be purified by dissolving it in ether and shaking the solution repeatedly with water, drying, and evaporating to dryness. The clear oil dissolved completely in concentrated hydrochloric acid, and was precipitated on dilution with water.

The *isonitroso*-acid itself did not reduce Fehling's solution, but, after boiling with dilute hydrochloric acid, gave all the tests for hydroxylamine. On treatment with bromine water, pyridine, and hydrogen peroxide (Piloty's test, *Ber.*, 1902, **35**, 3099), it was converted into a blue compound, which could be extracted by ether.

When heated in a vacuum, the *isonitroso*-acid decomposed, giving a white sublimate; the latter is strongly acid, and when extracted with boiling water yields, somewhat tardily, crystals, which melt sharply at 148°; this product was compared with a sample of the α -nitrile of camphoric acid prepared from *isonitrosocamphor* and acetic anhydride, and found to be identical with it.

It is noteworthy that α -ketohomocamphoric acid, its oxime, and also α -camphonitrile, are all difficult to obtain in stable, crystalline forms. This is possibly connected with the presence of the group $\cdot\dot{\text{C}}\text{H}$ in direct attachment to $>\text{CO}$, $>\text{C}:\text{NOH}$, and $\cdot\text{CN}$ respectively, combinations which are associated with the ready occurrence of isodynamic (tautomeric) change.

Action of Ferrous Hydroxide and Alkali on the Acid A₁.



Whilst most of the common reducing agents attack the acid A₁, either not at all or only with difficulty, the substance is very readily reduced by the following process.

The acid (5 grams) is dissolved in 20 per cent. potassium hydroxide (150 c.c.), the solution then added to one of crystallised ferrous sulphate (20 grams) in water (100 c.c.), and the whole heated at the boiling point for three hours. Some ammonia is evolved, and the dark precipitate finally becomes pale brown. After filtration, the clear, aqueous solution is acidified with hydrochloric acid and repeatedly extracted with ether, which, after drying and evaporating, furnishes about 4.2 grams of a white solid. The quantity of ammonia liberated in the foregoing operation was found to correspond with about 10 per cent. of the nitrogen present in the substance used; the nitrogen-free product has not been isolated.

The white solid, obtained as above, is best crystallised from acetone; from the cold solvent it separates in slender needles, which, if at once removed and dried, may be kept unaltered for some considerable time. If they are left in contact with the mother liquor, however, they soon become converted into plates, which represent the stable form of the compound.

The needle form, if heated, appears to undergo crystalline change at 190–200°, and subsequently liquefies at 230°; if heated suddenly to a high temperature, the needles do not melt instantaneously below about 234°, so that it is probable that their true melting point is somewhat higher even than this. The mass obtained by allowing the fused substance to solidify usually melts at about 205°, but it is uncertain what significance should be attached to this observation (Found: C=62.2; H=8.0; N=6.6. C₁₁H₁₇O₃N requires C=62.6; H=8.1; N=6.6 per cent.).

The equivalent, determined by titration with sodium hydroxide,

using phenolphthalein, was 210; a monobasic acid, $C_{11}H_{17}O_3N$, requires 211.

The molecular weight was determined in phenol by the cryoscopic method, the number obtained being 205 (mean of three determinations) instead of 211, as calculated.

α-Camphidonecarboxylic acid is insoluble in light petroleum, moderately soluble in ether or water, and freely so in alcohol, ethyl acetate, acetic acid, or chloroform. Its solubility in water is greatly raised by the addition of hydrochloric acid.

The aqueous solution is strongly acid and gives no coloration with ferric chloride. An aqueous solution of the sodium salt gives no precipitate with salts of silver, lead, mercury, copper, calcium, barium, or iron; it rapidly discharges the colour of permanganate and bromine water.

The free acid is exceedingly stable. It is not affected by boiling 50 per cent. sulphuric acid or potassium hydroxide, or by heating in a sealed tube with concentrated hydrochloric acid at 180° . In small quantities, it can be distilled with only slight decomposition. It is not readily oxidised by chromic acid mixtures, and does not appear to react with acid chlorides, with nitrous acid, or with methyl sulphate.

It was ultimately found possible to eliminate the carboxyl group by heating the *silver* salt. The latter was prepared by neutralising the acid in aqueous solution with silver carbonate, and formed long, colourless needles, which darkened on exposure to light; when cautiously heated in an atmosphere of carbon dioxide under diminished pressure, it decomposed and yielded a yellow sublimate. The latter was basic, and gave a characteristic picrate (m. p. $189-191^\circ$), which was purified by crystallisation, decomposed, and the free base recrystallised from light petroleum. The base formed arborescent leaflets melting at 230° (Found: C=71.7; H=10.2; N=8.2. $C_{10}H_{17}O_4N$ requires C=71.9; H=10.1; N=8.4 per cent.).

The characters of the base were almost precisely those ascribed to *α-camphidone* by Tafel and Eckstein (*Ber.*, 1901, **34**, 3280). Samples of the substance and its picrate were prepared from camphorimide, and direct comparison left no doubt as to the complete identity with the products above described.

The authors gratefully acknowledge that a grant from the Research Fund of the Chemical Society was used in defraying part of the expense of the work.

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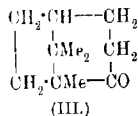
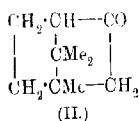
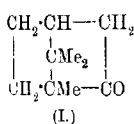
[Received, May 20th, 1920.]

LXXIX.—*Homocamphor*.

By ARTHUR LAPWORTH and FRANK ALBERT ROYLE.

CAMPHOR (I) and the large group of compounds closely related to it have attracted an unusual amount of interest, owing to the difficulty with which they yielded up the secrets of their exact structures. The varied changes to which the molecules of these substances are prone are not less remarkable because the gross results of such transformations can now be represented graphically; and although analogies may be drawn between their transformations and those in some other series, little is yet known of their mechanism. Again, although several ketones nearly allied to camphor have been prepared, these have not, for the most part, been very closely investigated, and therefore peculiarities in the behaviour of camphor have not yet been clearly associated with irregularities in structure; it is not clear, for instance, what is the precise influence exerted by the methyl groups, or what would be the effect of a change in the size of the carbon rings. Epicamphor (II) is unique as an instance of a compound which is very closely related to camphor, and has been experimentally compared with camphor in nearly all interesting particulars (Bredt and Perkin, T, 1913, 103, 2182).

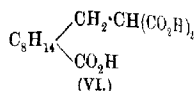
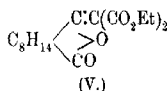
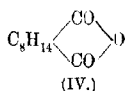
In 1913, the authors had in view the desirability of studying a substance differing from camphor in one particular only, namely, in the inclusion of an additional $\cdot\text{CH}_2\cdot$ group in the ketone ring. This substance they have prepared, and propose to term *homocamphor* (III). It was originally hoped to make the research a



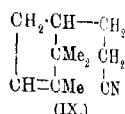
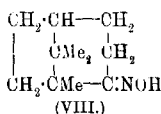
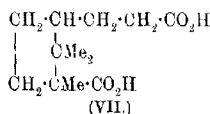
fairly exhaustive one, but it was found that the preparation of homocamphor in sufficient quantity would be a very lengthy and costly undertaking, and the conditions which have succeeded the outbreak of war, when the work was interrupted, have made the project impracticable for the present. It has therefore been decided to describe the results which have already been obtained.

The first step in the synthesis of homocamphor consisted in the preparation of camphorylmalonic ester (V) from camphoric

anhydride (IV) and diethyl sodiomalonate by Winzer's method (*Annalen*, 1890, 257, 298).



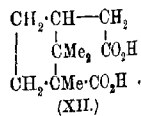
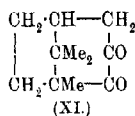
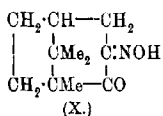
By reduction of (V) (best carried out electrolytically under the conditions referred to in the experimental part) and subsequent hydrolysis, hydrocamphorylmalic acid (VI) is obtained, and this is readily converted, on distillation, into carbon dioxide and Winzer's hydrocamphorylacetic acid (VII). The latter can be converted into homocamphor either by heating its lead salt in a current of carbon dioxide or by prolonged action of acetic anhydride, followed by distillation in a vacuum. Homocamphor



forms a colourless, indefinitely crystalline mass closely resembling camphor in odour, taste, and in general behaviour towards solvents. Its optical rotatory power is, however, in the opposite sense to that of the camphor from which, through camphoric anhydride and the above series of reactions, it is prepared; it has $[\alpha]_D -112.9^\circ$ in benzene, whilst camphor has $[\alpha]_D +39.1^\circ$.

Homocamphor readily yields a *semicarbazone* and an *oxime* (VIII). The latter closely resembles camphoroxime, and has much the same peculiar odour as that substance; like camphoroxime, it develops a perfume resembling that of raspberries when heated with sulphuric acid, and this is doubtless due to the formation of homocamphenonitrile (IX). This product does not appear to be formed so readily as is camphenonitrile from camphoroxime, which fact seems to indicate a greater stability of the six-carbon ring as compared with the five-carbon ring in camphoroxime.

An *isonitroso*-derivative (X) may be obtained from homocamphor under conditions similar to those used in converting camphor into its *isonitroso*-derivative, and closely resembles the latter in properties. By the action of acid formaldehyde on *isonitroso*homocamphor



(compare Lapworth, T., 1896, 69, 323), a small quantity of a volatile, yellow compound is obtained, and this much resembles camphorquinone, although it appears to be less intensely coloured; it is doubtless *homocamphorquinone* (XI).

In order to establish the structure of homocamphor, which in the absence of further data would have rested on the assumptions that Winzer's hydrocamphorylacetic acid has the structure (VII), and that no change of structure had attended the ring-closure at the succeeding step in the synthesis, advantage was taken of the ease with which cyclic isonitroso-ketones, like isonitrosocamphor, undergo the Beckmann change, becoming converted into amides or imides of the open-chain dicarboxylic acids. *isoNitrosohomocamphor* was warmed with acetyl chloride, and the product hydrolysed with alkali; as was anticipated, *homocamphoric acid* (XII) was precipitated on addition of acid, so that there can be no question that the structures assumed for homocamphor (III) and its isonitroso-derivative (X) are correct.

EXPERIMENTAL.

Camphorylmalonic ester was prepared by the condensation of ethyl sodiomalonate with camphoric anhydride in benzene, in accordance with Winzer's method (*loc. cit.*). It was obtained as a viscid, colourless liquid distilling at 218°/20 mm., and ultimately setting to a solid, which melted at 81° after recrystallisation from benzene. The yield fluctuated between 70 and 75 per cent. Attempts to shorten the time required for the condensation process by substituting toluene for benzene as solvent were not successful, and a trial of substituting camphoryl chloride for camphoric anhydride (Winzer, *loc. cit.*) did not give encouraging results.

For the reduction of camphorylmalonic ester, comparative tests of several methods were made. Winzer used sodium amalgam, allowing this to act on an alcoholic solution of the unsaturated ester, with such intermittent additions of sulphuric acid as were required to maintain a slightly acid reaction in the solution. He does not give the yield. In using this method, the present authors found that a decided improvement was effected by omitting the additions of sulphuric acid and employing instead a constant stream of carbon dioxide.

Much trouble was at first experienced in obtaining the hydrocamphorylmalonic acid in crystalline form, and the cause of this was ultimately traced to the fact that during the reduction the hydrolysis of the ester is not by any means so complete as Winzer's description would lead one to infer, and appreciable quantities of

the mono- and di-ethyl esters of hydrocamphorylmalonic acid are invariably left. It is therefore necessary, after the reduction itself is complete, to add to the solution a considerable excess of alkali and to heat for some time; when a portion of the liquid on acidification yields an acid which solidifies at once, the whole may be worked up in the usual manner. With these precautions, the authors were able to obtain yields of pure hydrocamphorylmalonic acid corresponding with 66 per cent. of that theoretically possible.

Many experiments were also made with the view of effecting the reduction electrolytically. A pure lead sheet, 20×30 cm., carefully polished, cleaned, and then covered with a deposit of spongy metal, was employed as cathode, and a sheet of platinum foil 5×2.5 cm. as anode. A clean, porous porcelain cell was used to contain the anode liquid (dilute sulphuric acid), and this was immersed in a beaker containing the cathode liquid. Glass spirals, through which cold water circulated, were immersed in the electrode chambers, and served for cooling purposes. The cathode liquid contained the unsaturated ester (20 grams) dissolved in a mixture of spirit (1500 grams) and concentrated sulphuric acid (150 grams). A current of 2 amperes at 10 volts was employed until reduction was complete, when the cathode liquor was completely hydrolysed with excess of alkali and worked up for hydrocamphorylmalonic acid. By this process, yields of 85 per cent. of the theoretical were normally obtained, but, like other similar reduction processes, success is uncertain unless the utmost care is exercised to ensure the purity of the fluids, electrodes, and cells.

Aluminium amalgam, used as reducing agent in diluted alcohol, gave yields of hydrocamphorylmalonic acid amounting to only 57 per cent. of the theoretical. Other methods of reduction, including the use of gaseous hydrogen and colloidal palladium, proved even less satisfactory.

The crude hydrocamphorylmalonic acid obtained by any of the above processes was converted into hydrocamphorylacetic acid by heating for an hour in an oil-bath at 180° , and then distilling in a vacuum; the fraction boiling at $260-270^{\circ}/20$ mm. yielded, as a rule, the pure hydrocamphorylacetic acid, melting at 142° , on recrystallisation from water. Occasionally, however, the product contained an impurity of an unsaturated character, in which case it was dissolved in sodium carbonate and left in contact with excess of permanganate for an hour, when it was subsequently recovered in satisfactory condition.

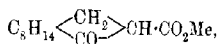
Dimethyl Hydrocamphorylacetate.

As one of the carboxyl groups of hydrocamphorylacetic acid is attached to a quaternary carbon atom, and is therefore resistant to the ordinary esterification processes, the dimethyl ester of the acid was prepared through the normal silver salt. The latter was readily obtained as an insoluble precipitate on addition of silver nitrate to the aqueous solution of the neutral sodium salt. The washed salt, dried at 110° , was boiled for three hours with methyl iodide dissolved in dry ether. The resulting ester was worked up in the usual manner, the main fraction being obtained as a colourless, viscid oil boiling at $175^{\circ}/20$ mm. Found: C=65.5; H=9.6. $C_{18}H_{24}O_4$ requires C=65.6; H=9.4 per cent.).

By cooling in liquid air and allowing the temperature slowly to rise, the oil set to a crystalline mass melting at about 25° .

An acid by-product, doubtless the *monomethyl* ester, was isolated during the working up of the diethyl ester; it distilled at $202-212^{\circ}/19$ mm. as a viscid, colourless oil which, when the interior of the containing tube was scratched with a glass rod, solidified to a mass of small needles.

When the above dimethyl ester is heated with excess of sodium methoxide at about 100° , the whole becomes brownish-red. On subsequently acidifying the solution, there is obtained a product which with ferric chloride gives a red coloration, soluble in amyl alcohol, and a copper derivative which is insoluble in water but soluble in alcohol. These facts point to the presence in this product of methyl homocamphorcarboxylate,



but this substance, from which it was hoped to prepare homocamphor, has not been closely examined, as the desired end was ultimately attained by a shorter route.

Homocamphor (III. p. 743).

This substance was obtained from hydrocamphorylacetic acid by the following processes:

(1) The acid was converted into its neutral sodium salt, and this, by double decomposition in aqueous solution with lead acetate, into the lead salt, which forms a heavy, white precipitate, and may be collected, washed with water and alcohol successively, and dried at 100° .

Ten grams of this salt were placed in a wide, hard-glass tube, which was slowly heated in an inclined position while a current of carbon dioxide was led through it from the higher end. The lower end of the tube was connected by means of an adapter to a flask, which served as a receiver, the issuing gases from the latter being passed through ether in order to retain the last traces of homocamphor. The crude product, after carefully evaporating off the ether used to collect it all, was a pale brown solid, and was purified by distillation in a current of steam.

(2) Homocamphorylacetic acid (8 grams) was boiled with acetic anhydride (20 grams) for several hours, and then allowed to remain at the ordinary temperature for some days. The acetic anhydride was subsequently removed by distillation, and the residue slowly heated under diminished pressure (12–20 mm.), the semi-solid distillate being warmed with aqueous sodium carbonate and distilled in a current of steam.

Homocamphor forms a white, indistinctly crystalline mass. In appearance, odour, and behaviour towards the usual media, it very closely resembles ordinary camphor, and, like that compound, is appreciably soluble in water, to which it communicates a camphoraceous odour. It was analysed after exposure in a vacuum desiccator over sulphuric acid (Found: C=79.3; H=10.9. $C_{11}H_{18}O$ requires C=79.5; H=10.9 per cent.).

Homocamphor melts at 189–190°, and sublimes readily far below this temperature. It is levorotatory, and has $[\alpha]_D -112.9^\circ$ in 4 per cent. solution in benzene.

Homocamphorsemicarbazone, $C_{11}H_{18}N \cdot NH \cdot CO \cdot NH_2$.

This is readily obtained by boiling homocamphor in alcoholic solution with semicarbazide hydrochloride and sodium acetate for three hours. It crystallises from alcohol in slender, colourless needles melting and decomposing at 250–252°. The substance is very sparingly soluble in water, but dissolves readily in methyl or ethyl alcohol. Cold concentrated hydrochloric acid dissolves it, and, on adding water, the semicarbazone is precipitated unchanged; but, if steam is passed through the solution, pure homocamphor passes over.

Homocamphoroxime (VIII, p. 744).

This is prepared by dissolving homocamphor (1 gram) in alcohol, adding solid hydroxylamine hydrochloride (0.8 gram) and sodium acetate (2–5 grams), and boiling the whole for two hours on the

water-bath. On cooling and diluting with water, the oxime is slowly deposited in crystals, which are collected and recrystallised from dilute methyl alcohol (Found: C=73.3; H=10.7; N=7.9. $C_{11}H_{19}ON$ requires C=72.9; H=10.5; N=7.7 per cent.).

This oxime much resembles camphoroxime in general behaviour towards organic solvent media, and has much the same peculiar odour as that substance. It crystallises from dilute methyl alcohol in long needles melting at 167–168°. When a small quantity of the oxime is heated with a drop of concentrated sulphuric acid, an odour very similar to that of campholenitrile becomes perceptible: the quantities of material available did not admit of the product being isolated.

isoNitrosohomocamphor (X, p. 744).

Homocamphor (3 grams) is dissolved in anhydrous ether (100 c.c.), and finely powdered sodamide (2 grams) is then added. The whole is stirred mechanically for two hours, then cooled to 0°, and maintained at this temperature while freshly distilled amyl nitrite (4.5 c.c.) is gradually introduced. After remaining overnight, the product is poured into ice-water, the aqueous layer separated, extracted repeatedly with ether, and then acidified with acetic acid. The precipitated solid (2 grams) is collected, washed with water, dried, and crystallised from a mixture of benzene and light petroleum.

The substance dissolves in all the usual organic media, and crystallises from water in long, slender needles, and from benzene and petroleum in small, flat plates. It melts at 167–168°.

It dissolves in formaldehyde (40 per cent.), and if the solution is warmed on the water-bath for two hours and then heated with excess of hydrochloric acid under a reflux condenser, minute, pale yellow crystals, which have a sweet, camphoraceous odour, collect in the condenser tube; these crystals doubtless consist of *homocamphorquinone* (XI, p. 744). The rate of formation of this compound is not so rapid as that of ordinary camphorquinone from *isomitosocamphor* in similar circumstances (compare Lapworth, *loc. cit.*), and as the yield was very small, sufficient could not be obtained for accurate characterisation or analysis.

Conversion of isoNitrosohomocamphor into Homocamphoric Acid.

isoNitrosohomocamphor (0.5 gram) was boiled with acetyl chloride for five hours, the solution then evaporated to dryness, and the solid residue boiled with 40 per cent. aqueous potassium hydroxide

for ten hours, during which time ammonia was slowly evolved. After a preliminary extraction with ether to remove neutral material, the alkaline liquid was acidified with sulphuric acid. The resulting brown acid which was precipitated proved to be highly insoluble in most of the ordinary organic media, but dissolved freely in boiling nitrobenzene, and, on cooling, separated in microscopic needles melting at 233° ; its equivalent, determined by titration against $N/10$ -sodium hydroxide, using phenolphthalein as indicator, was 106. The characters described are precisely those of *homocamphoric acid* (XII, p. 744), the calculated equivalent of which is 107.

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LXXX.—*The Nitration of Aceto-m-toluidide.*

By JAMES WILFRED COOK and OSCAR LISLE BRADY.

FROM the nitration products of *m*-toluidine, only 6-nitro-*m*-toluidine has been isolated, although evidence has been obtained that at least two of the other possible isomerides are formed in small quantities. Nitration in the presence of excess of concentrated sulphuric acid does not lead to meta-substitution. From aceto-*m*-toluidide, the 4- and 6-nitro-*m*-toluidines have been isolated, and this result has been confirmed by the present authors.

The dinitration of aceto-*m*-toluidide should, theoretically, give rise to three isomerides, and the reaction has been studied with the view of obtaining moderate quantities of 2:6-dinitro-*m*-toluidine for the synthesis of 2:3:6-trinitrotoluene.

Aceto-*m*-toluidide is added in small quantities at a time to ten times its weight of nitric acid (D 1.5) with thorough agitation, the temperature being kept below 25° ; on pouring into water, a mixture of the dinitroaceto-*m*-toluidides separates as a pasty mass. This cannot be recrystallised satisfactorily, so is converted into a mixture of the amines by heating on the water-bath for an hour with 50 per cent. sulphuric acid, filtering off any tarry matter through glass wool, and diluting the filtrate with

water. The precipitated amines are collected, washed and dried, when a product is obtained which sinters at 90° and melts completely at 150°.

Separation of the Dinitro-m-toluidines.—The mixture of dinitro-*m*-toluidines is fractionally recrystallised from alcohol. The first fraction which separates from the hot alcohol melts at 170°, on diluting somewhat with water a second fraction melting at 145° is obtained and on completely precipitating the filtrate a third fraction melting at 92–93°.

By further recrystallisation of these fractions and combining the products of higher melting point, a compound melting at 193–194° is obtained, which proved to be 4:6-dinitro-*m*-toluidine. Its identity was established by the mixed melting-point method with the compound obtained by the action of ammonia on 3:4:6-trinitrotoluene (Hepp, *Annalen*, 1882, **215**, 371). This compound was not oriented by Hepp, and is incorrectly given as a derivative of *p*-toluidine in Richter's "Lexicon." The correct formula is assigned to it by Will (*Ber.*, 1914, **47**, 708), who obtained from it 2:4-dinitrotoluene by removal of the amino-group. The compound has also been oriented by one of us in several ways.

The fractions of lower melting point could not be separated by recrystallisation from alcohol, acetic acid or benzene, but if they are acetylated with acetic anhydride and the dinitroaceto-*m*-toluidides recrystallised from alcohol, 2:6-dinitroaceto-*m*-toluidide (m. p. 163°; Körner and Contardi, *Atti R. Accad. Lincei*, 1916, [v], **25**, ii, 339) separates first and can readily be obtained pure.

The identity of this compound was confirmed by hydrolysis to the amine (m. p. 131° crude; Körner and Contardi, *loc. cit.*, give 133.8°), removal of the amino-group by the diazo-reaction and identification of the 2:6-dinitrotoluene obtained by the mixed melting-point method.

No 2:4-dinitro-*m*-toluidine has been isolated from the nitration product and from a consideration of the relative solubilities of the three dinitro-*m*-toluidines and of their acetyl derivatives, and of the course of the fractional crystallisation of the mixture, it seems probable that little, if any, of this compound is formed in the nitration of aceto-*m*-toluidide.

In one experiment, on recrystallising the acetyl compounds from the fractions of lower melting point, a compound melting at 228–230° was the main product and this proved to be slightly impure 2:4:6-trinitroaceto-*m*-toluidide. It was thought that 2:4-dinitro-*m*-acetotoluidide might be more readily nitrated than the other isomerides, and for this reason not appear as such in the product; experiment has shown that this compound is not

nitrated under the conditions of experiment, and that more vigorous treatment leads to decomposition.

Nitration of 6-Nitroaceto-m-toluidide.—6-Nitroaceto-m-toluidide was at first prepared by Cohen and Dakin's method (T., 1903, 83, 33), but later a modification was introduced which simplified the separation of the two isomerides formed.

To a mixture of 100 c.c. of nitric acid (D 1.5) and 25 c.c. of glacial acetic acid, cooled in ice, 20 grams of aceto-m-toluidide are added. After an hour, the mixture is poured into $1\frac{1}{2}$ litres of water and the solid which separates is collected at once. This melts at 101–102° and is almost pure 6-nitroaceto-m-toluidide, one crystallisation from alcohol yielding the pure substance. The filtrate, on remaining overnight, deposits more crystals which melt at 68–75°, one recrystallisation from alcohol giving pure 4-nitroaceto-m-toluidide.

The 6-nitroaceto-m-toluidide is added to excess of nitric acid (D 1.5), the temperature being kept below 25°, the mixture allowed to remain for an hour and poured into water. The pasty solid is extracted with ether, the ethereal solution washed with water, the solvent removed and the residue hydrolysed with 50 per cent. sulphuric acid. The amines, after precipitation by dilution, are separated in a manner similar to that described above. In this way 4:6- and 2:6-dinitroaceto-m-toluidides are obtained.

2:4- and 4:6-Dinitro- and 2:4:6-Trinitro-aceto-m-toluidides.

These compounds have been prepared for the purpose of identifying the various acetyl compounds obtained in the above reaction. They are obtained by warming the corresponding amines with acetic anhydride in the presence of one drop of concentrated sulphuric acid, pouring the product into water and recrystallising the precipitated acetyl derivative from alcohol.

2:4-Dinitroaceto-m-toluidide crystallises in colourless needles melting at 211–212°:

0.2895 gave 45.3 c.c. N_2 at 20.5° and 745 mm. $N=17.9$.

$C_9H_9O_5N_2$ requires $N=17.6$ per cent.

4:6-Dinitroaceto-m-toluidide crystallises in pale yellow needles melting at 103°:

0.2167 gave 33.8 c.c. N_2 at 18° and 746 mm. $N=18.0$.

$C_9H_9O_5N_2$ requires $N=17.6$ per cent.

2:4:6-Trinitroaceto-m-toluidide crystallises in microscopic, white, silky needles melting and decomposing at 249°:

0.1029 gave 17.8 c.c. N_2 at 18° and 751 mm. $N=19.9$.

$C_9H_8O_7N_4$ requires $N=19.7$ per cent.

Summarising, the main product of the dinitration of aceto-*m*-toluidide and of the nitration of 6-nitroaceto-*m*-toluidide is 4:6-dinitroaceto-*m*-toluidide. A smaller quantity of the 2:6-dinitro-compound is formed and little, if any, of the 2:4-dinitro-derivative.

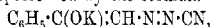
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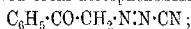
LXXXI.—*Studies in the Camphane Series. Part XXXVIII. The Cyanohydrazone of Camphorquinone.*

By MARTIN ONSLOW FORSTER and WILLIAM BRISTOW SAVILLE.

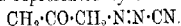
ALTHOUGH the aliphatic diazo-compounds have received increasing attention during recent years, their behaviour towards potassium cyanide has not been systematically studied. Peratoner and Palazzo (*Atti R. Accad. Lincei*, 1907, [v]. **16**, ii, 432, 501) noted the production of acetonitrile and methylcarbamine from diazomethane and hydrogen cyanide, whilst Wolff (*Annalen*, 1902, **325**, 149) found that diazoacetophenone and potassium cyanide gave a product which he represented by the formula



and regarded as derived from acetophenoneazocyanide,



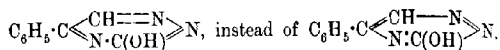
he also described it as yielding "acetophenoneazocarbamide," $\text{C}_6\text{H}_5\cdot\text{CO}\cdot\text{CH}_2\cdot\text{N}\cdot\text{N}\cdot\text{CO}\cdot\text{NH}_2$, with boiling dilute sulphuric acid. In a subsequent paper with Lindenhayn (*Ber.*, 1903, **36**, 4126), the possibility of acetophenoneazocyanide being phenylglyoxalcyano-hydrazone, $\text{C}_6\text{H}_5\cdot\text{CO}\cdot\text{CH}\text{:N}\cdot\text{NH}\cdot\text{CN}$, was indicated, but evidently not preferred, by Wolff, because in a much later paper with Greulich (*Annalen*, 1912, **393**, 41) the corresponding product from diazoacetone was represented by the formula



Diazocamphor being now a convenient material in which to observe the behaviour of the diazo-group, we have prepared from it by the action of potassium cyanide a compound which can scarcely be other than the cyanohydrazone of camphorquinone, because it dissolves in sodium carbonate and is hydrolysed very readily by acids to the α -semicarbazone. It seems to follow that the alternative grouping, $\text{CH}\cdot\text{N}\cdot\text{N}\cdot\text{CN}$, adopted by Wolff is

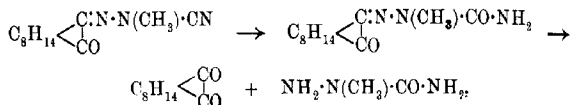
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excluded, and that his "acetophenoneazocarbamide" is really phenylglyoxalsemicarbazone, the phenylhydroxytriazine derived from it being, therefore,

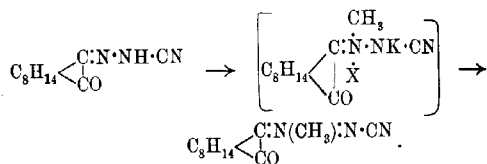


It is thus 5-phenyl-3-oxy-1:2:4-triazine, strictly comparable with 5:6-diphenyl-3-oxy-1:2:4-triazine prepared by Thiele and Stange (*Annalen*, 1894, **283**, 27) from benzilsemicarbazone, and with camphaneoxytriazine from camphorquinone- β -semicarbazone (Forster and Zimmerli, T., 1910, **97**, 2176).

Unfortunately, the readiness with which the cyano-group in the cyanohydrazone undergoes hydrolysis has precluded the isolation of cyanohydrazine, $\text{NH}_2 \cdot \text{NH} \cdot \text{CN}$, which was one of the objects of our inquiry. Moreover, finding that a methyl derivative is readily obtained from the cyanohydrazone, and thus hoping to arrive at methylecyanohydrazine, $\text{NH}_2 \cdot \text{N}(\text{CH}_3) \cdot \text{CN}$, we encountered another unforeseen obstacle. Not only did the cyano-group undergo hydrolysis with equal readiness, but the methylsemicarbazide obtained by complete hydrolysis of the camphorquinonemethylcyanohydrazone is not 2-methylsemicarbazide, as would be expected from the changes,



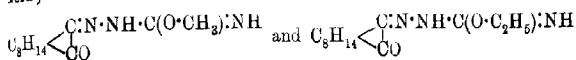
but an isomeric substance melting at 91.5° instead of 113° . In view of the indifference towards benzaldehyde shown by this isomeride, the only conclusion to be drawn is that it is the missing 1-methylsemicarbazide, $\text{CH}_3 \cdot \text{NH} \cdot \text{NH} \cdot \text{CO} \cdot \text{NH}_2$, and that methylation of the cyanohydrazone has proceeded as follows:



Support is given to this conjecture by the fact that whilst the cyanohydrazone is colourless and has $[\text{M}]_D^{25} 574^\circ$, the methyl derivative is bright yellow and has $[\text{M}]_D^{25} 1460^\circ$; since the α -semicarbazone with $[\text{M}]_D^{25} 619^\circ$ and the methylsemicarbazone are also colourless, it is reasonable to conclude that the cyanohydrazone, which

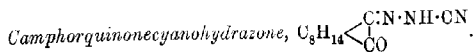
passes into the semicarbazone so readily, is closely allied to it in structure, and that this has become modified in methylation. Some analogy to such a change is offered by the alkylation of oximes, the products of which may be referred to both types, $C:NOH$ and $C:NH:O$.

When hydrolysis of camphorquinonecyanohydrazone is effected with mineral acids in methyl or ethyl alcohol, the α -semicarbazone is accompanied by a basic material, the composition of which is that of the cyanohydrazone increased by the elements of the alcohol employed. These compounds are indifferent towards alcoholic potassium hydroxide or benzoyl chloride, but are converted into camphorquinone and its semicarbazone by hydrochloric acid; this behaviour and origin suggest that the bases are



representing a new class of compounds, namely, imino-ethers of a semicarbazone.

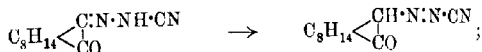
EXPERIMENTAL.



Whilst diazocamphor is completely transformed into the potassium derivative of the cyanohydrazone when an alcoholic solution remains for several days in contact with finely powdered potassium cyanide, action is more expeditious when the salt is dissolved in the minimum quantity of water. A solution containing 20 grams of diazocamphor in 100 c.c. of alcohol was therefore mixed with 25 grams of potassium cyanide in 50 c.c. of water, alcohol being then added in quantity just sufficient to form a clear liquid. After four days, the solution was diluted largely with water and extracted three times with ether, the faintly yellow, aqueous portion being then deprived of the major part of its ether-content by cold exhaustion during one hour at the water-pump. Acidification with dilute hydrochloric acid precipitated the cyanohydrazone in glistening, almost colourless crystals, the filtrate, which still contained ether, depositing a small additional quantity on keeping; the product weighed 19 grams. If the partial removal of ether prior to precipitation is omitted, addition of acid separates an ethereal layer, which maintains the cyanohydrazone in solution, besides impairing the quality of the product. The substance was purified by dissolution in $2\frac{1}{2}$ parts of acetone, to which 6 parts of petroleum (b. p. 65°) were then added, pearly leaflets being precipitated; it becomes red at 141° , evolves gas at 204° , and a few

degrees above this temperature melts indefinitely to a red liquid (Found: C=64.53; H=7.27; N=20.52. $C_{11}H_{15}ON_3$ requires C=64.39; H=7.31; N=20.49 per cent.). The cyanohydrazone dissolves in alkali carbonates, and is readily soluble in organic media, excepting petroleum. A solution containing 0.3005 gram in 25 c.c. of 10 per cent. sodium carbonate gave α_D 4921' in a 1-dcm. tube, whence $[\alpha]_D$ 361.9°, which did not change during five weeks when protected from light; on exposure, however, the liquid rapidly became yellow and turbid. When examined immediately, a solution containing 0.3000 gram in chloroform diluted to 25 c.c. gave α_D 3921' in a 1-dcm. tube, rising during nine days to 3937', and subsequently falling; thus, the rotatory power in this solvent varies between $[\alpha]_D$ 279.1° and 301.4°. In alkaline solution, the cyanohydrazone is reduced by zinc dust or sodium "hydrosulphite" to aminocamphor (identified as the benzoyl derivative), but it does not couple with benzenediazonium chloride.

The yellow compound into which the cyanohydrazone changes when the solid, or its solution in sodium carbonate, is exposed to light, appears to be the isomeride arising from the transformation



it crystallises from alcohol in silky, yellow needles containing the solvent, and was therefore precipitated from benzene by petroleum (Found: C=64.18; H=7.43). The substance becomes red at 182°, evolving gas at 189°, and passing to a viscous, red liquid at 193°; it yields camphorquinone when heated with dilute sulphuric acid.

The methyl derivative of the cyanohydrazone was prepared by shaking 20 grams dissolved in 80 c.c. of 10 per cent. sodium carbonate with 12 grams of methyl sulphate, and separated after thirty minutes in sulphur-yellow needles, weighing 19 grams; it melts at 135° after recrystallisation from methyl alcohol, separating in lustrous, transparent, six-sided plates (Found: C=65.29; H=7.85; N=19.26. $C_{12}H_{17}ON_3$ requires C=65.75; H=7.76; N=19.18 per cent.). It crystallises from boiling water in long, pale yellow needles, and is not volatile in steam. A solution containing 0.2000 gram in chloroform diluted to 25 c.c. gave α_D 5920' in a 1-dcm. tube, whence $[\alpha]_D$ 666.6°.

The benzoyl derivative, prepared by the Schotten-Baumann process, crystallises from alcohol in long, colourless, striated plates melting at 155° (Found: N=13.71. $C_{15}H_{19}O_2N_3$ requires N=13.59 per cent.). A solution containing 0.2016 gram in chloroform diluted to 25 c.c. gave α_D 2925' in a 1-dcm. tube.

whence $[\alpha]_D$ 299.6°. Under conditions which led to hydrolysis of the cyanohydrazone, the benzoyl derivative remained unchanged.

The *acetyl* derivative was produced in the course of two days when the cyanohydrazone remained suspended in two parts of acetic anhydride, and, after crystallisation from glacial acetic acid, melts at 104° (Found: N=16.98. $C_{18}H_{17}O_2N_3$ requires N=17.00 per cent.). A solution containing 0.2048 gram in chloroform diluted to 25 c.c. gave α_D 2°50' in a 1-dcm. tube, whence $[\alpha]_D$ 345.8°.

Attempts to prepare benzyl, *p*-toluenesulphonyl, and hydroxy-ethyl derivatives of the cyanohydrazone were unsuccessful.

Action of Acids on Camphorquinonecyanohydrazone.

The course of hydrolytic change undergone by the cyanohydrazone varies materially with experimental conditions. Thus cold concentrated sulphuric acid liberates gas, whilst 50 per cent. acid produces hydrazine and camphorquinone in a few minutes when warmed. With oxalic acid in hot alcohol, the α -semicarbazone of camphorquinone is formed, and this arises also when the cyanohydrazone, dissolved in alcohol, remains during several days with hydrochloric or sulphuric acid; simultaneously, there is formed a basic substance, melting at 79.5°, when ethyl alcohol is used, and a lower homologue, melting at 133°, along with azocamphanone when methyl alcohol is the solvent.

Twenty grams of the cyanohydrazone dissolved in 30 grams of alcohol were left with 32 grams of concentrated hydrochloric acid during ten days, in which period there separated lustrous, colourless plates, augmented to 5.8 grams by dilution with water; this was identified with the α -semicarbazone by complete analysis and a melting point of the mixture. The quantity obtained from 10 grams of the cyanohydrazone in 20 grams of alcohol with 15 grams of sulphuric acid was very small, but a 50 per cent. yield was produced by hydrochloric acid when methyl in place of ethyl alcohol was used.

The Accompanying Bases.—On rendering alkaline with sodium carbonate the filtrate from semicarbazone, there was precipitated a yellow, granular *base*, weighing 8 grams in the above experiment with hydrochloric acid and 7 grams in that with sulphuric acid, which is thus more favourable to its production. After being twice recrystallised from alcohol diluted with water, it melts at 79.5°, separating in long, lustrous, pale yellow needles (Found: C=62.06; H=8.46; N=16.73. $C_{13}H_{21}O_2N_3$ requires C=62.15; H=8.36; N=16.73 per cent.). A solution containing 0.2000 gram in chloroform diluted to 25 c.c. gave α_D 2°14' in a 1-dcm. tube,

whence $[\alpha]_D^{279.1^\circ}$. The substance is indifferent towards alcoholic potassium hydroxide, but when warmed with hydrochloric acid yields a mixture of camphorquinone with the α -semicarbazone; a suspension in sodium hydroxide is unchanged by benzoyl chloride.

The homologue was prepared by carefully mixing the cyanohydrazone (10 grams) dissolved in methyl alcohol (20 grams) with concentrated sulphuric acid (15 grams). After one week, liberal dilution with water precipitated a small amount of azocamphanone, the filtrate giving a deep yellow, viscous product when rendered alkaline. This was washed and set aside for many weeks, during which time it gradually became friable, and was then extracted several times with hot petroleum (b. p. 65°), which removed a very small quantity of a yellow, crystalline material melting at 86° . A solution of the residue in cold methyl alcohol was diluted with water until turbid, and the clear liquid decanted next day from an oily deposit; a yellow, solid *base* then separated, and melts at 133° after recrystallisation from methyl alcohol (Found: C=60.95; H=8.27; N=17.66. $C_{15}H_{16}O_2N_2$ requires C=60.76; H=8.01; N=17.72 per cent.). A solution containing 0.2023 gram in chloroform diluted to 25 c.c. gave α_D^{209} in a 1-dm. tube, whence $[\alpha]_D^{265.7^\circ}$.

Hydrolysis of the Methyl Derivative of Camphorquinonecyanohydrazone.

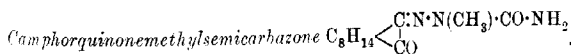
The conditions which produce the α -semicarbazone from the cyanohydrazone did not lead to the corresponding methyl derivative from the methylated cyanohydrazone; instead, the hydrazine residue appears to be removed in the form of 1-methylsemicarbazide, associated with a *compound* having the empirical formula of the original methyl derivative, but melting at 101° .

The methyl derivative (10 grams) in alcohol (30 grams) was left with anhydrous oxalic acid (4.1 grams) during ten days, when the solution had deposited colourless, silky needles (0.65 gram). These having been filtered, liberal dilution with water precipitated a yellow, viscous product (6.8 grams), from which steam removed camphorquinone (1.4 grams); by treatment with alcohol, the sticky residue yielded a pale yellow substance, which melts at 101° after crystallisation from petroleum (Found: C=66.08; H=8.05; N=19.01. $C_{15}H_{17}ON_3$ requires C=65.75; H=7.76; N=19.17 per cent.). This product yielded camphorquinone with hydrochloric acid, and its formation was not observed when the methyl derivative was heated with oxalic acid in alcohol under reflux instead of remaining at the ordinary temperature. Thus the former pro-

cedure is preferable for obtaining the 1-methylsemicarbazide *oxalate*, 1·2 grams of which was produced from 6·6 grams of the methylated cyanohydrazone. It is freely soluble in water, from which alcohol precipitates it in colourless, silky needles; it melts and effervesces at 171° (Found: N=23·74. $C_3H_7ON_3 \cdot C_2H_2O_4$ requires N=23·46 per cent.).

1-Methylsemicarbazide was isolated by heating the oxalate in water with calcium carbonate until effervescence ceased, evaporating the filtrate to dryness, and extracting the residue with boiling benzene, which deposited colourless, pearly leaflets melting at 91·5° (Found: N=47·01. $C_3H_7ON_3$ requires N=47·19 per cent.). It rapidly gives a mirror with ammoniacal silver oxide, and reduces Fehling's solution on boiling, but it does not combine with benzaldehyde. The oxalate was also obtained by decomposing the methyl derivative of the cyanohydrazone (10 grams) in alcohol (40 grams) with sulphuric acid (5 grams) at the ordinary temperature, diluting largely after ten days, filtering from camphorquinone (2·6 grams), neutralising with barium carbonate, and evaporating the filtrate until pasty; on dissolving in alcohol and adding oxalic acid, the oxalate (0·7 gram) slowly separated.

Attempts to prepare 1-methylsemicarbazide by indirect methods for comparison with the foregoing product were unsuccessful. Benzylidenesemicarbazone (which melts at 225°, instead of 214° as stated in the literature) could not be methylated by methyl sulphate in boiling benzene or in cold alkali, and the action of benzoyl chloride in pyridine led to *s*-benzoylbenzylidenedehydrazine, $C_6H_5 \cdot CH:N \cdot NH \cdot CO \cdot C_6H_5$, melting at 208° (Found: C=75·18; H=5·45; N=12·50. Calc.: C=75·00; H=5·35; N=12·50 per cent.). On the other hand, when acetonesemicarbazone is treated with benzoyl chloride in pyridine, the product is benzoylsemicarbazide, melting at 222°. In this connexion, it should be mentioned that the *oxalate* of 2-methylsemicarbazide, prepared for comparison with the foregoing salt, melts and effervesces at 155° (Found: N=31·69. $(C_3H_7ON_3)_2 \cdot C_2H_2O_4$ requires N=31·34 per cent.). It crystallises from hot water in transparent prisms, and is very sparingly soluble in alcohol.



Having regard to the abnormal behaviour of camphorquinone-cyanohydrazone on methylation, brought to light by the production of 1-methylsemicarbazide on hydrolysing the product, it was thought desirable to methylate the α -semicarbazone. Action in this case is normal, the methylated semicarbazone being identical

with the substance obtainable from camphorquinone by condensation with 2-methylsemicarbazide.

The α -semicarbazone (4.7 grams), dissolved in 10 per cent. sodium hydroxide (10 c.c.) and sufficient water to form a clear solution, was shaken with methyl sulphate (4 grams), when a colourless solid (4.6 grams) was precipitated. Being very soluble in alcohol, liberal dilution with water was necessary before it crystallised in colourless, triangular plates; it melts and evolves gas at 176° , and rapidly becomes bright yellow on exposure to light. In view of the misleading results of analysis, which pointed at first to a dimethyl derivative, the same compound was prepared also from camphorquinone (6 grams) and 2-methylsemicarbazide (3.3 grams) in alcohol, when it was found to contain water of crystallisation (Found: C = 58.17, 58.27; H = 8.18, 8.27; N = 17.07. $C_{12}H_{10}O_2N_{3.5}H_2O$ requires C = 58.54; H = 8.13; N = 17.07 per cent.). A solution containing 0.2051 gram in chloroform diluted to 25 c.c. gave $n_D^{20} 1.3930$ in a 1 cm. tube, whence $[\alpha]_D 426.6^\circ$. On hydrolysis with aqueous sulphuric acid and removal of camphorquinone by ether, the remaining liquid gave benzylidenemethylsemicarbazone (m. p. 162°) with benzaldehyde.

Further Changes undergone by Diazocamphor.

Concurrently with the foregoing, attempts have been made to bring diazocamphor into combination with various agents likely to attack the diazo-group. For instance, it seemed probable that

the triketone, $C_8H_{14} \begin{array}{c} \diagup \text{CCl} \cdot \text{CO} \cdot \text{CCl} \diagdown \\ \text{CO} \quad \text{OC} \end{array} C_8H_{14}$, or, alternatively, the

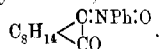
chloride of chlorocamphorcarboxylic acid, $C_8H_{14} \begin{array}{c} \diagup \text{CCl} \cdot \text{COCl} \\ \text{CO} \end{array}$, might

arise by the action of carbonyl chloride, since Staudinger has found that diphenyldiazomethane is thus converted into diphenylchloroacetyl chloride (*Ber.*, 1916, **49**, 1939); although nitrogen is disengaged slowly, however, the action leads only to Angeli's camphenone, the ketone produced on heating diazocamphor. The constitution of this has been recently shown by Bredt and Holz (*J. pr. Chem.*, 1917, [ii], **95**, 133) to be that of a β -pericyclo-camphanone. Unsuccessful, also, were attempts to couple the diazo-group with, or to displace it by, nitromethane, ethyl malonate, picryl chloride, or phenylacetonitrile.

It has been already observed (T., 1910, **97**, 2171) that ammonium sulphide reduces diazocamphor to a mixture of the α - and β -hydrazones of camphorquinone; other reducing agents, such as sodium "hydrosulphite," stannous chloride in ether, an aluminium-mercury

couple, and aluminium in sodium hydroxide, transform it into camphor. In view of a recent paper by Staudinger and Miescher (*Helv. Chim. Acta*, 1919, **2**, 554), who obtained nitrones of the general formulæ $R\cdot CH:NX'O$ and $R_2\cdot C:NX'O$ by the action of aromatic nitroso-derivatives on aliphatic diazo-compounds, we heated diazocamphor with nitrosobenzene, obtaining camphoryl-*N*-phenylnitron (isonitrosocamphor-*N*-phenyl ether), corresponding with the *N*-methyl (T., 1904, **85**, 896) and the *N*-ethyl (T., 1908, **93**, 251) ethers already prepared from sodium isonitrosocamphor and the alkyl iodides. Attempts to produce analogous derivatives from nitrosodimethylaniline, nitrosodiphenylamine, and nitrosocarbazole failed.

The N-Phenyl Ether of isoNitrosocamphor,



Diazocamphor (4.5 grams) and nitrosobenzene (2.6 grams) were heated together at 65° until gas evolution became brisk, when the tube was withdrawn and cooled; the diminished action was alternately stimulated and checked until it was safe to heat the mixture continuously. The deep green colour gradually faded to pale brown, and when gas no longer emerged, the product was set aside until crystals appeared. These were augmented by adding petroleum, from which the substance was recrystallised in lustrous, yellow needles melting at 78° (Found: C=74.48; H=7.63; N=5.53. $C_{16}H_{18}O_2N$ requires C=74.71; H=7.39; N=5.44 per cent.). A solution containing 0.2037 gram in chloroform, diluted to 25 c.c., gave α_D 0°45' in a 1-dm. tube, whence $[\alpha]_D$ 92.0°. Reduction with aluminium-mercury in ether gave phenylamino-camphor.

In conclusion, we desire to express our thanks to the Managers of the Royal Institution for their courtesy in placing a laboratory at our disposal.

SALTERS' INSTITUTE OF INDUSTRIAL CHEMISTRY,
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[Received, May 12th, 1920.]

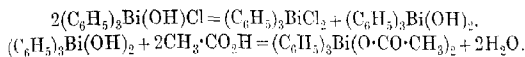
LXXXII.—*Organo-derivatives of Bismuth. Part III.*
The Preparation of Derivatives of Quinquevalent Bismuth.

By FREDERICK CHALLENGER and ARCHIBALD EDWIN GODDARD.

WITH the object of preparing salts of the unknown compounds Ph_3BiO or $\text{Ph}_3\text{Bi}(\text{OH})_2$, the action of aqueous potassium hydroxide and moist silver oxide on triphenylbismuthine dichloride has been investigated under various conditions. In all cases, triphenylbismuthine is regenerated. The same result is obtained if the dibromide is treated with alcoholic sodium hydroxide. Triphenylstibine dibromide when similarly treated yields triphenylstibine dihydroxide (Michaelis and Reese, *Annalen*, 1886, **233**, 50). If the solution obtained from triphenylbismuthine dichloride and aqueous alkali is treated with acetic, tartaric, or a similar organic acid, mixtures are obtained which contain dichloride and basic chloride, and very little, if any, acetate or tartrate. Better results were obtained with the carbonate described, but not analysed, by Michaelis and Marquardt (*Annalen*, 1889, **251**, 330). This compound with acetic acid gives *triphenylbismuthine acetate*, $\text{Ph}_3\text{Bi}(\text{OAc})_2$. The corresponding camphorsulphonate and lactate appear to be formed, and are now under investigation. With hydriodic acid, the carbonate reacts at the ordinary temperature, with the formation of a red compound, which is probably the one already described by Challenger and Allpress (*T.*, 1915, **107**, 21). Similar results were obtained by triturating the carbonate with water and iodine. This is further evidence of the instability of triphenylbismuthine diiodide, which cannot be prepared from triphenylbismuthine and iodine. Triphenylbismuthine dichloride dissolves in cold concentrated sulphuric acid, giving *triphenylbismuthine sulphate*, which does not melt at 284° . Very little bismuth sulphate is produced in this reaction if rise of temperature is avoided, but the amount increases if the solution in sulphuric acid is left for several hours before pouring into water. Solution in ammonia and treatment with hydrochloric acid converts the sulphate into the *basic chloride*, which, on warming with concentrated hydrochloric acid, gives the dichloride. The basic chloride, $\text{Ph}_3\text{Bi}(\text{OH})\text{Cl}$ (m. p. 160 — 161°), is formed in various reactions, for example, (a) by the action of moist ammonia gas on triphenylbismuthine dichloride in chloroform solution (a method by which the *basic bromide*, m. p. 150 — 151° , has also been prepared);

b) from sodium and the dichloride in ether containing a trace of moisture; (c) by the action of aqueous ammonia on the dichloride. Up to the present, however, this compound has not been obtained from the dichloride by means of water or aqueous alcohol, according to which method Stulp* (*Diss.*, Rostock, 1910) prepared the basic bromides of tri-*p*-tolyl- and trixylyl-bismuthines.

When warmed with concentrated hydrochloric acid, it gives the dichloride. The action of acetic acid on the basic chloride gives rise to the dichloride and a compound, which is probably the acetate, in which case the reaction may be represented thus:



This is analogous to the action of acetic acid on the basic bromide of diphenyltelluride, $\text{Ph}_2\text{Te}(\text{OH})\text{Br}$, which gives rise to the dibromide, and probably the diacetate (Lederer, *Annalen*, 1912, 391, 335).

With magnesium methyl iodide, the basic chloride does not give triphenylmethylbismuthonium hydroxide, $\text{Ph}_3\text{Bi}(\text{OH})\text{CH}_3$, but the dichloride and triphenylbismuthine, which points to the instability of the hydroxide. Triphenylmethylarsonium hydroxide, however, is a crystalline compound melting at 125—126°, prepared by the action of moist silver oxide on the iodide (Michaelis, *Annalen*, 1902, 321, 166).

The action of copper bronze on triphenylbismuthine dichloride leads to the production of diphenylchlorobismuthine, probably owing to the prolonged action of heat, and not to contact with the copper. No compound of the type $\text{Ph}_3\text{Bi}:\text{BiPh}_3$ was isolated.

In this connexion, it is worthy of note that triphenyl- and tri-*p*-tolyl-bismuthines and arsines, and also tri- α -naphthylbismuthine and triphenylbismuthine dichloride, have the normal molecular weight in benzene solution. Complexes of the type $\text{R}_3\text{M}:\text{MR}_3$, which might possibly arise owing to the unsaturated nature of these organo-metallic or metalloid compounds, do not appear to be formed.

The abnormal behaviour of the halogen derivatives of the bismuthines towards the Grignard reagent has been referred to in previous papers.† It is further exemplified by the fact that triphenylbismuthine is the principal product obtained when

* The results described in this dissertation do not appear to have been published elsewhere.

† Better results may possibly be obtained by modifying the conditions of reaction with the Grignard reagent, or by the use of organo-zinc or mercury derivatives. Experiments in this direction are in progress.

magnesium *p*-tolyl bromide reacts with triphenylbismuthine dichloride and diphenylbromobismuthine, and in the reaction between triphenylbismuthine dichloride and magnesium α -naphthyl bromide. Lederer (*Ber.*, 1911, **44**, 2287) has shown that triphenyltelluronium chloride yields diphenyltelluride and diphenyl when treated with magnesium phenyl bromide, whilst di-*o*-anisyltelluride dibromide is reduced to di-*o*-anisyltelluride on treatment with magnesium methyl iodide [*Ber.*, 1920, **53**, 713]. Compare also the remarkable instability of the mixed mercury diaryls (Hilpert and Grüttner, *Ber.*, 1915, **48**, 406)].

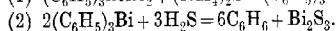
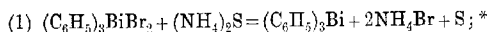
Iodine trichloride reacts with triphenylbismuthine, producing the dichloride and iodobenzene.

Tri- α -naphthylbismuthine dichloride was prepared by the action of chlorine on the bismuthine; Stilp (*loc. cit.*) was unable to obtain this compound. Like triphenylbismuthine dichloride, it is more stable than the corresponding dibromide.

The action of moist silver oxide in acetone is similar to that observed with triphenylbismuthine dichloride, and gives rise to tri- α -naphthylbismuthine.

Diphenyl- α -naphthylbismuthine has been previously described (T., 1914, **105**, 2216). Since attempts to obtain other mixed bismuthines have failed, the reaction between diphenylbromobismuthine and magnesium α -naphthyl bromide has been further studied. Whilst the mixed bismuthine has again been obtained and diphenyl- α -naphthylbismuthine dibromide analysed, the main product of the reaction consists of triphenylbismuthine.

Michaelis and Marquardt (*Annalen*, 1889, **251**, 320) observed that excess of ammonium sulphide decomposed triphenylbismuthine dibromide according to the equations:



We have found that this reaction can be made the basis for the estimation of bismuth in substances of an analogous composition which, unlike the tertiary bismuthines, do not yield bismuth chloride with hydrochloric acid.

Triphenylstibine dihaloids do not react thus with hydrogen sulphide in alcoholic ammonia, but yield triphenylstibine sulphide. The bismuthine is therefore less stable than the corresponding stibine.

* In the absence of excess of hydrogen sulphide the bismuthine only is obtained.

EXPERIMENTAL.

Action of Moist Silver Oxide on Triphenylbismuthine Dichloride.

(a) *In the Cold.*—Two grams of triphenylbismuthine dichloride, about 30 c.c. of acetone, 0.93 gram of silver oxide, and 1 c.c. of water were shaken on a machine for sixteen hours, when 1.1 grams of triphenylbismuthine (m. p. 78°) were obtained from the acetone solution. The residue consisted of silver oxide, silver chloride, and a trace of bismuthine.

(b) *At about 60° .*—Five grams of triphenylbismuthine dichloride and 2.3 grams of silver oxide were heated in moist acetone on a water-bath for one hour. After removing the silver chloride and unchanged silver oxide, 3.2 grams of triphenylbismuthine were obtained.

Action of Alcoholic Potassium Hydroxide on Triphenylbismuthine Dichloride.

(a) *In the Cold.*—Three grams of triphenylbismuthine dichloride and 0.7 gram of potassium hydroxide in absolute alcohol were shaken for five and a-half hours.

Two kinds of crystals separated on keeping, (a) stout needles, and (b) small, fine needles mixed with a heavy powder, which were extracted with absolute alcohol, leaving potassium chloride. The alcoholic extract yielded triphenylbismuthine (m. p. $78-80^{\circ}$). The crystals (a) were found to be triphenylbismuthine dichloride.

The main bulk of the mixture was evaporated, when more triphenylbismuthine was obtained.

(b) *At the Boiling Point.*—Five grams of triphenylbismuthine dichloride in absolute alcohol were boiled for three hours with 1.2 grams of potassium hydroxide, and the solution filtered. From the filtrate, three deposits, (a), (b), and (c), were obtained. The crystals (a) melted at 138° , contained halogen, and most probably consisted of a mixture of triphenylbismuthine, triphenylbismuthine dichloride, and the basic chloride (see p. 768).

Deposit (b) was shaken with cold light petroleum; the extract deposited triphenylbismuthine, the insoluble portion yielding unchanged dichloride (m. p. $120-121^{\circ}$).

Deposit (c) was heated with water, the soluble portion yielding triphenylbismuthine (m. p. 78°); the insoluble residue consisted chiefly of potassium chloride.

Action of Aqueous Potassium Hydroxide on Triphenylbismuthine Dichloride.

Three grams of triphenylbismuthine dichloride, 0.7 gram of potassium hydroxide, and 30 c.c. of water were shaken in the cold for five and a-half hours, and the mixture was filtered. The residue was triphenylbismuthine dichloride. The filtrate was evaporated to dryness and treated with absolute alcohol, which removed potassium chloride. The solution was evaporated, and the residue, after crystallisation from light petroleum, melted at 77–78°, and did not depress the melting point of triphenylbismuthine.

Attempts to Isolate Triphenylbismuthane Dihydroxide or Triphenylbismuthine Oxide.

(1) Triphenylbismuthine dichloride was treated with aqueous potassium hydroxide in the cold as before, and the solution extracted three times with ether. The extract became cloudy on keeping, possibly owing to the absorption of atmospheric carbon dioxide. A solid finally separated which, on crystallisation from petroleum, melted at 74°. This was shown to be impure triphenylbismuthine. The aqueous portion also became cloudy and deposited triphenylbismuthine, which melted at 78–79° after crystallisation from alcohol. No compound corresponding with a dihydroxide or oxide was isolated.

(2) Triphenylbismuthine dibromide was dissolved in alcoholic sodium hydroxide, and the precipitate of sodium bromide filtered off. No further deposit was noticed after the solution had remained for a week. Part of the alcohol was therefore evaporated, when long needles of triphenylbismuthine were deposited.

Preparation of Michaelis's so-called Basic Carbonate.

Triphenylbismuthine dibromide (m. p. 122–124°) was suspended in alcohol and treated with excess of solid sodium hydroxide. Carbon dioxide was passed through the solution, the voluminous, white precipitate collected, and the operation repeated until no further deposit was formed. The solid was washed with much cold water, and appeared to be free from halogen. In order to free it from adhering alkali carbonate, it was boiled with water, but even after continued boiling it gave the flame reaction for sodium. This trace of impurity probably accounts for the low

percentages of carbon obtained in the analyses. It did not melt at 220° (Found: C=44.40, 44.16; H=3.01, 3.07; Bi=41.87, 41.45. $C_{39}H_{15}O_3Bi$ requires C=45.68; H=3.03; Bi=41.67 per cent.).

It is evident from these results that the compound which Michaelis described as a basic carbonate, $Ph_3BiO + CO_2$, is in reality the normal carbonate, Ph_3BiCO_3 .

Triphenylbismuthine carbonate is insoluble in ordinary organic solvents; different preparations varied in colour from pure white to pale yellow. With concentrated hydrochloric acid, effervescence took place, and triphenylbismuthine dichloride (m. p. 126°) was obtained.

Action of Glacial Acetic Acid on Triphenylbismuthine Carbonate.

Three grams of triphenylbismuthine carbonate were dissolved in a small quantity of glacial acetic acid by the aid of heat. Carbon dioxide was evolved, and, on cooling and adding a small quantity of water, a white precipitate was obtained, which was collected and washed with light petroleum, air being drawn through until the solid no longer had the odour of acetic acid. The substance melted sharply at 162° , and on crystallisation from water and acetic acid had the same melting point. The yield was 3.3 grams (Found: C=47.06, 47.58; H=3.86, 3.72; Bi=37.31, 37.13. $C_{22}H_{21}O_4Bi$ requires C=47.39; H=3.79; Bi=37.32 per cent.).

Triphenylbismuthine acetate is a white powder completely soluble in glacial acetic acid or ethyl acetate on warming. It is readily soluble in cold chloroform or nitrobenzene and in xylene on warming, moderately so in warm benzene, acetone, carbon tetrachloride, or alcohol, and insoluble in water or light petroleum.

If the acetic acid solution of the acetate is allowed to remain for several days without addition of water, long, transparent needles separate, which soften at 130° and melt at 136 – 137° (Found: Bi=35.16, 35.36. $C_{22}H_{21}O_4Bi \cdot \frac{1}{2}C_2H_4O_2$ requires Bi=35.43 per cent.).

If this substance is triturated with water, the acetate (m. p. 162°) is obtained, which, if dissolved in acetic acid and allowed to crystallise, again yields the acid acetate.

Action of Hydriodic Acid and Iodine on Triphenylbismuthine Carbonate.

Hydriodic acid, containing as usual a little free iodine, was added to the carbonate; a red compound was immediately formed and an odour of iodobenzene noticed. The red product appeared to be a mixture.

The same result was obtained when the carbonate was triturated with an aqueous solution of iodine.

Action of Sulphuric Acid on Triphenylbismuthine Dichloride.

Triphenylbismuthine dichloride (6 grams) was added during fifteen minutes, with constant shaking, to 20 c.c. of sulphuric acid maintained at about 10° . Hydrogen chloride was evolved, and a clear solution obtained, through which air was drawn for three hours to remove dissolved hydrogen chloride, after which the mixture was poured on ice. The precipitated solid (5.3 grams) was well washed with water, dried, extracted twice with boiling chloroform, and washed with ether. The acid wash waters contained inorganic bismuth, from which, however, the solid was free (Found: Bi = 38.60; S = 6.10. $C_{18}H_{15}O_4SBi$ requires Bi = 38.80; S = 5.98 per cent.).

Triphenylbismuthine sulphate is a white solid not melting below 280° , and is very sparingly soluble in the usual organic solvents.

Action of Moist Ammonia Gas on Triphenylbismuthine Dichloride.

Nine grams of triphenylbismuthine dichloride were dissolved in chloroform containing a little light petroleum. Moist ammonia gas was passed in, the solution became cloudy, and soon deposited a white solid. This was collected, and the operation repeated until no more solid separated. The deposit was washed with cold water until all ammonium chloride was removed. Washing was then continued with boiling water. This produced violent frothing of the solid, and chloroform was evolved, the latter probably being present as chloroform of crystallisation. When no further effervescence was noticed, the residue was dried on porous porcelain, and then in the air. It melted at $156-158^{\circ}$, and, after crystallisation at $160-161^{\circ}$, the latter figure being unaltered after repeated recrystallisation. Two separate preparations were analysed (Found: Cl = 7.25, 7.20; Bi = 42.34, 42.54. $C_{18}H_{15}OCl_2Bi$ requires Cl = 7.21; Bi = 42.31 per cent.).

Triphenylbismuthine hydroxychloride is a white powder insoluble in water or light petroleum, moderately soluble in ether, acetone, benzene, or xylene, completely so in alcohol or nitrobenzene on heating, and readily so in cold chloroform.

The derivative containing chloroform was not analysed, since the combined solvent was liberated on keeping in air or drying in a vacuum.

Action of Sodium on Triphenylbismuthine Dichloride in Ether.

Five grams of triphenylbismuthine dichloride and 1 gram of sodium were suspended in ether and heated on a water-bath for nine hours, and the product was filtered. The filtrate, on keeping, deposited crystals melting at 160–162°, which did not depress the melting point of triphenylbismuthine hydroxychloride. The sodium in the residue was destroyed by alcohol, and the remaining solid extracted with acetone, when sodium chloride was left, and the solution gave a further quantity of hydroxychloride. The production of this compound was probably due to a trace of moisture in the ether.

Action of Water on Triphenylbismuthine Dichloride.

Two grams of triphenylbismuthine dichloride were dissolved in alcohol, the solution was poured into a large excess of water, and evaporated slowly to dryness. The residue was evaporated with water several times, and the melting point of the product was unchanged. No hydroxychloride, hydroxide, or oxide had thus been formed.

Action of Glacial Acetic Acid on Triphenylbismuthine Hydroxychloride.

Two grams of triphenylbismuthine hydroxychloride were dissolved in glacial acetic acid by the aid of heat. On cooling, a solid was deposited, which melted sharply at 142°. This was boiled with acetone and filtered. On cooling the filtrate, crystals appeared (m. p. 152–153°), containing bismuth and organic matter, but, no halogen. Recrystallisation from chloroform and then alcohol gave products melting at 146–148° and 152–153°, probably impure triphenylbismuthine acetate (m. p. 162°).

The acetone mother liquors deposited well-defined crystals melting at 128–130° after recrystallisation from alcohol. Further crystallisation gave long needles (m. p. 126°), which did not depress the melting point of triphenylbismuthine dichloride.

The residue left from the acetone extraction of the product, melting at 142°, fused at 136–138°, and was shaken with cold chloroform, in which it was completely soluble. This solution was carefully investigated, but only unchanged basic chloride (m. p. 160–161°) and a small amount of a viscid residue could be isolated.

Action of Magnesium Methyl Iodide on Triphenylbismuthine Hydroxychloride.

Triphenylbismuthine hydroxychloride (1.2 grams) was added to a solution of 0.05 gram of magnesium and 0.3 gram of methyl iodide in dry ether; an orange coloration appeared, which persisted for some time. Next day the mixture was heated on a water-bath for five hours and filtered. The residue contained practically no organic matter. The main ethereal solution was evaporated, when two distinct types of crystals separated, together with a trace of oil. The crystals were washed with warm alcohol; the residue contained halogen, melted at 125—126°, and did not depress the melting point of triphenylbismuthine dichloride. The alcoholic solution yielded triphenylbismuthine. Since no trace of the iodine was discovered, it was probably contained in the oil, which was too small in quantity for further investigation.

Action of Moist Ammonia Gas on Triphenylbismuthine Dibromide.

The preparation was carried out as in the case of the basic chloride, the crude product apparently containing chloroform of crystallisation, as before. After washing with hot water, it melted at 150—151°, and, after four recrystallisations, had a constant melting point of 147—148° (Found: Br = 15.44, 15.41; Bi = 38.43, 39.13. $C_{18}H_{10}OBrBi$ requires Br = 14.91; Bi = 38.79 per cent.).

The two preparations were made at an interval of several months, and the somewhat high halogen content seems to point to the presence of a trace of unchanged dibromide.

Triphenylbismuthine hydroxybromide is a yellow powder, insoluble in water, light petroleum, or ether, sparingly soluble in boiling acetone or benzene, moderately so in boiling toluene or xylene, and readily so in boiling alcohol or nitrobenzene and in cold chloroform.

Action of Copper Bronze on Triphenylbismuthine Dichloride.

Five grams of triphenylbismuthine dichloride and 0.6 gram of copper bronze were heated for eleven hours with dry acetone on a water-bath, and the solid was separated. On treatment of the concentrated acetone solution with light petroleum, triphenylbismuthine, a small amount of copper chloride, and diphenylchlorobismuthine (2.4 grams: m. p. 184—186°) were obtained, whilst the final residues had a strong odour of chlorobenzene.

The last two substances were probably formed from the dichloride by the prolonged heating, and not owing to the action of the copper.

Molecular Weights of some Bismuth and Arsenic Derivatives.

These determinations were carried out by the cryoscopic method in benzene solution.

Triphenylbismuthine.—0.2845 gave $\Delta = -0.153^\circ$. M.W. 427.
(C_6H_5)₃Bi requires 439.

Triphenylarsine.—0.2370 gave $\Delta = -0.179^\circ$. M.W. 298.9.
(C_6H_5)₃As requires 306.1.

Tri-p-tolylbismuthine.—0.2304 gave $\Delta = -0.115^\circ$. M.W. 458.3.
(C_7H_7)₃Bi requires 481.

Tri-p-tolylarsine.—0.3605 gave $\Delta = -0.241^\circ$. M.W. 342.8.
(C_7H_7)₃As requires 348.

Triphenylbismuthine Dichloride.—0.8847 gave $\Delta = -0.470^\circ$.
M.W. 498.5. (C_6H_5)₃BiCl₂ requires 509.5.

Tri- α -naphthylbismuthine.—0.1588 gave $\Delta = -0.122^\circ$. M.W. 577.
(C_{10}H_7)₃Bi requires 589.

All the above show normal values.

Action of Magnesium p-Tolyl Bromide on Triphenylbismuthine Dichloride.

The Grignard solution (1.1 mols.) was added to triphenylbismuthine dichloride suspended in ether, and the usual transient violet coloration observed. The whole was heated on a water-bath for three to four hours, when a granular precipitate settled out. After twelve hours, the ether was evaporated and the residue distilled in a current of steam. The product remaining in the distillation flask solidified (m. p. $72-73^\circ$), and was recrystallised four times from alcohol, giving crops melting at 76° , 78° , 78° , the last fraction being melted with triphenylbismuthine. The mother liquors were fractionally crystallised, but no product other than triphenylbismuthine could be isolated.

Action of Magnesium p-Tolyl Bromide on Diphenylbromobismuthine.

The reaction was carried out as above, and the mixture distilled in a current of steam; the residue melted at 70° , and was recrystallised three times from acetone, but in each case the crystals melted at 78° and gave the reactions of triphenylbismuthine. The mother liquors yielded a further quantity of triphenylbismuthine.

Action of Iodine Trichloride on Triphenylbismuthine.

Five grams of the bismuthine were dissolved in dry ether and 2.7 grams of iodine trichloride in the same solvent gradually added. A momentary red coloration appeared on mixing, and a pale brown oil separated out and soon solidified. The ethereal solution was evaporated, yielding an oil, which with chlorine in chloroform solution gave 0.4 gram of iodobenzene dichloride. The solid, after crystallisation from acetone and light petroleum, melted at 120° and did not depress the melting point of triphenylbismuthine dichloride.

Tri- α -naphthylbismuthine Dichloride.

Five grams of the bismuthine were dissolved in dry chloroform and treated with chlorine. The addition of light petroleum gave a yellow precipitate (4.6 grams: m. p. 158—159°), and the mother liquors yielded a further 0.7 gram. Recrystallisation twice from chloroform-petroleum solution gave a product melting sharply on both occasions at 166° (Found: Cl=10.68, 10.66; Bi=30.87, 30.84. $C_{30}H_{21}Cl_2Bi$ requires Cl=10.74; Bi=31.51 per cent.).

Tri- α -naphthylbismuthine dichloride is a yellow, crystalline powder readily soluble in chloroform, moderately so in acetone or benzene, and insoluble in light petroleum. On heating for several hours at 100°, it did not smelt of chloronaphthalene, was stable to hydrochloric acid, and melted at 167—169°.

Action of Moist Silver Oxide on Tri- α -naphthylbismuthine Dichloride.

The dichloride (2 grams) and silver oxide (0.7 gram) were suspended in moist acetone and well shaken. Reaction occurred almost at once, and, after two days, the mixture was filtered and the residue extracted with chloroform, which yielded two deposits of tri- α -naphthylbismuthine, 0.5 gram (m. p. 230°) and 0.2 gram (m. p. 232° on one crystallisation). Spontaneous evaporation of the acetone solution yielded a small amount of a brown solid, which became very viscid on warming with alcohol, had a strong odour of naphthalene, and was not further examined.

Diphenyl- α -naphthylbismuthine Dibromide.

Diphenyl- α -naphthylbismuthine (0.8 gram) was treated in dry chloroform-ether solution with a slight excess of bromine in chloro-

form. On addition of light petroleum, 0.81 gram of dibromide was precipitated (Found: Br=24.83; Bi=31.87. $C_{22}H_{17}Br_2Bi$ requires Br=24.59; Bi=31.99 per cent.).

Determination of the Metal in Derivatives of Quinquevalent Bismuth.

The substance (0.2—0.3 gram) was treated with about 10 c.c. of an ammoniacal solution of hydrogen sulphide, and the mixture vaporated to dryness in an air-bath at 115—125°, the benzene formed during the decomposition driven off, and the residue of bismuth sulphide and sulphur boiled for a few minutes with 10 c.c. of concentrated hydrochloric acid. The solution was filtered, diluted with water, hydrogen sulphide passed, and the precipitated bismuth sulphide filtered on a Gooch crucible, washed with carbon bisulphide, dried, and weighed.

The method was first tested on two well-known compounds, namely, triphenylbismuthine dichloride (Found: Bi=40.44. $C_{18}H_{15}Cl_2Bi$ requires Bi=40.78 per cent.) and dibromide (Found: Bi=34.92. $C_{18}H_{15}Br_2Bi$ requires Bi=34.73 per cent.).

Our thanks are due to the Research Fund of the Chemical Society for a grant which has defrayed the expenses of this investigation.

THE UNIVERSITY,
EDGBASTON, BIRMINGHAM.

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LXXXIII.—*Note on the Preparation of certain Iodo-compounds.*

By CUTHBERT WILLIAM JAMES, JAMES KENNER, and
WILFRID VICTOR STUBBINGS.

THE authors, having occasion to attempt the preparation of certain 2:6-derivatives of iodobenzene from the corresponding amino-compounds, were confronted with the well-known difficulty that a number of the latter are only very incompletely diazotised under the conditions usually employed. The yield, however, of iodo-compound obtained was usually very satisfactory when allowance was made for the proportion of amino-derivative unchanged. It therefore only remained to achieve complete diazotisation, and it was decided to apply the process specially recommended by Witt-

in such cases (*Ber.*, 1909, **42**, 2953), and consisting in the addition of a mixture of the base with a molecular proportion of potassium metabisulphite to fuming nitric acid. By pouring the product on ice, as described by Witt, and adding a solution of iodine in potassium iodide, extremely satisfactory yields of great purity were achieved in the cases of 2-iodoisophthalic acid, 2-iodo-3-nitrobenzoic acid, and 5-chloro-4-iodo-3-nitrotoluene. 5-Iodoisophthalic acid is more satisfactorily prepared by the ordinary process, which involves no difficulty as regards diazotisation. Attempts to prepare picryl iodide were unsuccessful, probably owing to instability of the diazonium compound, and the method is also obviously unsuitable for compounds like benzidine, which are easily nitrated.

When the diazotised solution, prepared by Witt's process from 3-nitroanthranilic acid, was added to a large excess of cuprous chloride solution, the product contained, besides the desired chloro-nitrobenzoic acid, a considerable amount of hydroxy-compound. Apparently, therefore, the method is unsuitable for the preparation of chloro-derivatives. For many purposes, however, iodo-compounds are at least equally suitable, and it was considered that the successful outcome of the experiments now described might more usefully be separately recorded than as an incident in the syntheses for which the compounds in question were required.

EXPERIMENTAL.

2-Iodoisophthalic Acid.

The starting point for the preparation of this compound was 2-nitro-*m*-toluic acid. The oxidation of this compound to 2-nitroisophthalic acid, referred to by Noelting and Gachot (*Ber.*, 1906, **39**, 73), by neutral potassium permanganate solution is only complete after the mixture has been boiled for some hours. Noelting and Gachot also describe the preparation of 2-aminoisophthalic acid from the nitro-acid by means of tin and hydrochloric acid; it is more conveniently carried out by the addition of stannous chloride to a suspension of the nitro-derivative in a boiling mixture of acetic and hydrochloric acids. The free amino-acid separates on cooling the solution.

The conversion of 2-aminoisophthalic acid into 2-iodoisophthalic acid was carried out by Mayer (*Ber.*, 1911, **44**, 2301), but, as he admits, the product was very impure. On repeating the process, which consisted in the very slow addition of a solution of the sodium salt of the acid and of sodium nitrite to dilute sulphuric acid, a purer product was obtained, but only about 25 per cent. of the material was diazotised after thirty hours. Witt's process

was therefore adopted, a finely ground mixture of aminoisophthalic acid (20 grams) and potassium metabisulphite (12.5 grams) being gradually added to fuming nitric acid (45 c.c.) below 10°. After four hours, the mixture was poured on ice (220 grams), and to the resulting clear solution was added a solution of iodine (17 grams) in potassium iodide (33 grams) in the minimum quantity of water. The product (29 grams) melted at 229°. By crystallisation from water, the melting point rose to 236—238°, but a determination of the equivalent showed the acid still to contain 5 per cent. of hydroxyisophthalic acid. Mayer gives a melting point of 205—222°, even after purification of the acid through its methyl ester. The probable explanation of the discrepancy became obvious when a small portion of the acid was submitted to hydrolysis by boiling alcoholic sodium hydroxide. As a result, pure hydroxyisophthalic acid, $C_6H_3(OH)(CO_2H)_2 \cdot H_2O$ (m. p. 244°; equivalent, 99.3), was obtained, and further characterised by its red coloration with ferric chloride.

3-Nitroanthranilic Acid.

3-Nitroaceto-*o*-toluidide was easily obtained by the addition of sulphuric acid (2 grams) to a mixture of 3-nitro-*o*-toluidine (20 grams) and acetic anhydride (26 grams). A clear solution resulted, accompanied by a rise in temperature to 70°, and almost immediately after the whole set to a mass of crystals, which were collected after the addition of water. The product (25.5 grams) melted at 156°, which was raised to 157—158° by recrystallisation from dilute acetic acid.

3-Nitroacetylanthranilic acid was prepared by oxidising 3-nitroaceto-*o*-toluidide (10 grams) at 100° with a solution of potassium permanganate (22 grams) and magnesium sulphate (16 grams) in water (1100 grams). For some unexplained reason, the melting point of the product (9 grams) varied considerably. By fractional crystallisation from dilute acetic acid, the product of several preparations was separated into two distinct substances, one in the form of stout, golden-yellow prisms (m. p. 244.5°), the other in yellow needles (m. p. 178°), which it is hoped to discuss in a subsequent communication.

By boiling 3-nitroacetylanthranilic acid, either the crude oxidation product or the separate compounds above described, for thirty-five minutes with 50 per cent. sulphuric acid (4 parts), almost pure 3-nitroanthranilic acid (m. p. 205°) is obtained in a yield of more than 90 per cent. The yield is diminished if the strength of acid or the duration of boiling is increased. The acid has been previously described by Hübner (*Annalen*, 1879, 195,

37), who obtained it in the form of its ester by the action of ammonia on ethyl 3-nitrosalicylate.

It is noteworthy that the esterification of the acid is only accomplished with difficulty under ordinary conditions. Thus, after the acid (10 grams) had been boiled with alcohol (50 c.c.) and sulphuric acid (5 c.c.) for twenty-four hours, 5 grams remained unchanged, and 5.8 grams of ester had been produced.

2-Iodo-3-nitrobenzoic Acid.

(a) When a suspension of 3-nitroanthranilic acid (10 grams) in sulphuric acid (11 grams) and water (53 grams) was diazotised in the usual manner, 5.5 grams of acid remained undissolved, whilst from the solution 7 grams of crude iodonitrobenzoic acid were obtained. A similar, but less satisfactory, result was obtained when the ester was used in place of the free acid.

(b) 202.5 Grams of nitrobenzoic acid, when submitted to the treatment already described in the case of aminoisophthalic acid, gave 321 grams of iodonitrobenzoic acid (m. p. $203-206^{\circ}$), a yield of 98 per cent. of the theoretical.

By crystallisation from water, the acid is obtained in prisms melting at 206° (Found: N=4.82. $C_7H_4O_4NI$ requires N=4.78 per cent.).

5-Chloro-4-iodo-3-nitrotoluene.

(a) In an experiment by Mr. C. W. Judd, from 15 grams of 5-chloro-3-nitro-*p*-toluidine, which had been treated with nitrous acid and potassium iodide in the usual manner, 9 grams were recovered unchanged, whilst 6.5 grams of chloriodonitrotoluene (m. p. 83°) were generated from the remainder.

(b) Three grams of the base, treated as described for 2-aminoisophthalic acid, gave 3.7 grams of iodo-derivative (m. p. 92°).

5-Chloro-4-iodo-3-nitrotoluene separates from light petroleum in plates melting at 92° , which are colourless when pure, but usually red (Found: N=4.85. $C_7H_5O_2NClI$ requires N=4.71 per cent.).

The authors wish to express their acknowledgments to the Research Fund Committee of the Chemical Society for a grant, to The British Dyestuffs Corporation for supplies of *o*-toluidine, and to Messrs. Whiffen and Sons for the iodide used in these experiments. Two of them (C. W. J. and W. V. S.) also wish to thank the Corporation for the opportunity of collaborating in this work.

THE UNIVERSITY,
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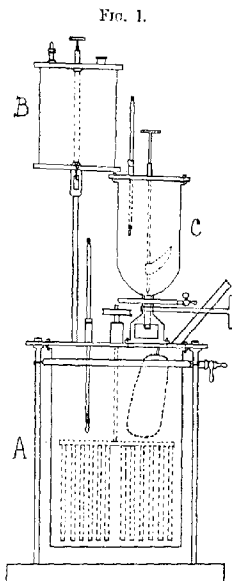
LXXXIV.—*Diphenylarsenious Chloride and Cyanide.*
(*Diphenylchloroarsine and Diphenylcyanoarsine.*)

By GILBERT T. MORGAN and DUDLEY CLOETE VINING.

THE employment of diphenylarsenious chloride as a military poison has led in recent years to many experiments on the preparation of this compound and its intermediates.

In one of these processes, triphenylarsine is the starting point, and this intermediate is produced by Michaelis's modification of the Fittig reaction, in which arsenious chloride, chlorobenzene, and sodium interact in an inert medium (La Coste and Michaelis, *Ber.*, 1878, 11, 1881; *Annalen*, 1880, 201, 215; 1881, 207, 195; 1902, 321, 160; Philips, *Ber.*, 1886, 19, 1031). As practised by these investigators, the process is unsuitable for large-scale operations. The introduction of the whole of the sodium at the commencement of the process renders the operation hard to regulate, and unless great care is taken, the condition of the metal as regards superficial oxidation is likely to vary considerably from one batch to another, so that the onset and course of the reaction are not easily controlled. Moreover, the sludgy form in which the sodium chloride is left at the end of the condensation when carried out under the earlier laboratory conditions leads to further difficulties in the separation of triphenylarsine. The sodium present in large excess at the commencement of the operation certainly sets up side reactions, leading to the formation of diphenyl and ill-defined arsenical products. In the small-scale plant illustrated in Fig. 1, these difficulties were obviated, and the whole operation could be completed without the addition of water, another factor which makes for safety.

The cylindrical, steel reaction vessel (3 litres capacity), fitted



with a steel cover rendered gas-tight with an asbestos washer, was supported by four upright steel rods fixed in a trough with a waste-pipe leading to the sink. Round the outside of the reaction vessel, and near the top, a perforated water-pipe was carried concentrically, and attached to the steel supports. By this means, a stream of cold water could be distributed over the outer surface of the reaction vessel, which could also be heated by a rose burner.

The cover of the reaction vessel, *A*, which was perforated to admit a thermometer, carried the following fittings:

(1) A central steel comb stirrer provided with a pulley for mechanical stirring.

(2) A water-cooled steel reflux condenser.

(3) A baffle plate projecting into the vessel to assist in the mixing of the contents and to prevent the rotating liquid from splashing up in the condenser.

(4) A sodium dropping apparatus, *C*, consisting of a cylindrical steel container (1 litre capacity) with a curved bottom perforated at its lowest point with an outlet hole (0.6 cm. in diameter). A steel tap and a sight-feed with transparent silica windows attached to the base of the container enabled the operator to regulate the flow of molten sodium.

A ring burner placed under the base of the sodium container just above the outlet tap was used to keep the metal in a molten condition. The steel cover of the container, made air-tight with an asbestos washer, carried a thermometer and a hand stirrer, shaped to scour the bottom of the container and provided with a sharp prong to dislodge any obstacle in the outlet tap.

(5) A cylindrical glass reservoir, *B*, for liquid (capacity, 800 c.c.) with steel ends, fitted with vertical outlet tube to reaction vessel, a needle valve regulated by a spindle, and a sight-feed with glass window. The steel cover of this reservoir was fitted with a screw-stoppered inlet and with a valve for introducing compressed air, so that the contained liquid was expelled under slight pressure.

Procedure.—Arsenious chloride (276 grams), chlorobenzene (510 grams), and xylene (400 c.c.) were mixed; half the liquid was placed in the reservoir and half in the reaction vessel, where it was diluted with 800 c.c. of xylene. Sodium (210 grams) was introduced into the sodium container and covered with xylene. The reaction vessel was heated to 70° and the sodium container to 110°. Stirring was commenced (speed of rotation, 250–300 revs. per minute), the sight-feed of the sodium apparatus warmed with a Bunsen burner, and molten sodium dropped into the reaction vessel, the rate being regulated by the lower thermometer, the

temperature of which was not allowed to rise above 70°. External cooling was applied when necessary.

After fifteen minutes, the solution from the liquid reservoir was allowed to flow in concurrently with the molten sodium. When all the reagents had been introduced, stirring was continued until the temperature began to fall without external cooling by water. The reaction vessel was then heated to 90° and allowed to cool. At 60° the mixture was filtered through a Bornett press, the granular precipitate of sodium chloride was washed with warm xylene, and afterwards exposed to the atmosphere until any traces of unaltered sodium had been oxidised. The filtrate was distilled up to 220° to remove solvent and chlorobenzene. The liquid residue, on cooling, changed to a pale yellow, crystalline mass of triphenylarsine (m. p. 58—59°). Yield, 383 grams=82 per cent.

The outstanding advantages of this process are as follows:

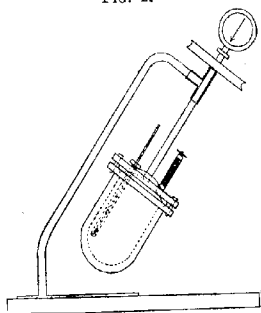
- (1) As sodium is never in excess during the reaction, the process is readily controlled.
- (2) Water is excluded from all stages of the preparation, thus eliminating danger from the explosive interaction of sodium and his liquid.
- (3) The salt residue is granular and easily filtered.
- (4) The product is obtained directly in a state of purity without further treatment.
- (5) Other coal-tar hydrocarbons, such as benzene or toluene, can be substituted for xylene as the working fluid in this plant without any material change in the procedure.
- (6) The foregoing apparatus can be employed with advantage for other applications of the Fittig reaction, the gradual addition of clean, unoxidised sodium being a useful improvement on the older processes.

Very favourable results were obtained in the preparation of triphenylstibine. Freshly distilled antimony trichloride (344 grams), chlorobenzene (510 grams), and xylene (400 c.c.) were mixed, and the solution was divided equally between reservoir and reaction vessel. In the latter case, 600 c.c. of xylene were added as diluent. Sodium (210 grams) covered with 500 c.c. of xylene was placed in the sodium container, and the process effected at 70° in the manner already described. After filtering off in the Bornett press the dark grey, granular sodium chloride, the filtrate, on distilling up to 220°, left a residue of triphenylstibine (m. p. 48—50°).

*The Rotating Autoclave.**I. Conversion of Triphenylarsine into Diphenylarsenious Chloride.*

This conversion was carried out in the rotating autoclave, a vessel formed by boring out the steel core of a 6-inch high-explosive shell until the thickness of the wall was about 1.9 cm. The steel cover, which was of similar thickness, was fastened down with twelve bolts and rendered gas-tight with a lead washer. The cover carried a powerful adjustable spring safety valve, a steel thermometer tube projecting into the cavity of the autoclave, and a hollow steel tube carrying an all-steel pressure gauge, which communicated with the interior of the vessel by means of a narrow, bored steel tube dipping into and protected by a concentric steel case partly filled with heavy oil, and having a small aperture at

FIG. 2.



its upper end for admitting the compressed gases from the autoclave. The pressure-gauge tube was fixed in the centre of the cover and fitted with a pulley, so that it also served as the axle of rotation for the autoclave, which was supported and spun in an inclined position. Rotating autoclaves have been made on these lines by Mr. H. Edenborough, of the Technical College, Finsbury, with capacities ranging from 500 c.c. to 9 litres.

The vessel used in the following experiments had a working capacity of 1 litre. A glass lining blown to fit into the cavity of the autoclave was employed in lieu of an enamelled lining.

Procedure.—Triphenylarsine (250 grams) was heated for three hours with 75 grams of arsenious chloride at 250–280°, the pressure attained being about 4.2–7 kilos. per sq. cm. The contents of the autoclave were then distilled in a current of carbon dioxide under a pressure of 20–30 mm., the following fractions being collected:

- (a) 150–190°: 68 grams, consisting of phenylarsenious dichloride with 32 per cent. of diphenylarsenious chloride.
- (b) 190–220°: 180 grams of diphenylarsenious chloride, 93 per cent.
- (c) 220–250°: 7 grams of triphenylarsine with 30 per cent. of diphenylarsenious chloride.

(d) Residue in still when extracted with chloroform yielded 17 grams of unchanged triphenylarsine.

Fraction (b) was cooled and drained, when it yielded 155 grams of colourless, crystalline diphenylarsenious chloride (m. p. 39—40°). The total yield of diphenylarsenious chloride was 66 per cent., of which 53 per cent. was isolated in a state of purity.

Fractions (a) and (c) and the triphenylarsine extracted from (d) were heated to 150° to remove volatile impurities, and returned to the autoclave for a subsequent operation, when 60 per cent. of this material was converted into crystalline diphenylarsenious chloride.

The residues from the second operation were available for further treatment, and the total yield of diphenylarsenious chloride was correspondingly increased. It was also found that 25 per cent. of this product could be frozen out from the contents of the autoclave without distillation.

By the foregoing dry processes, chlorobenzene and arsenious chloride can be converted into crystalline diphenylarsenious chloride without the intervention of water or the use of any aqueous reagent, the overall yield of this product being upwards of 60 per cent.

II. Diphenylarsenious Chloride from Phenylarsenious Dichloride.

The foregoing operations showed that the rotating autoclave can also be used with advantage in producing diphenylarsenious chloride from triphenylarsine obtained by the dry process, and phenylarsenious dichloride prepared by Bart's diazo-process (D.R.-P. 250264; Chem. Fabrik. von Heyden, D.R.-P. 264924).

These two reagents when heated for three hours at 250—280° gave a 60 per cent. yield of diphenylarsenious chloride, separated by the above-described fractional distillation.

III. Diphenylstibine Chloride.

Triphenylstibine, when heated with redistilled antimony trichloride for three hours at 250—280° in this autoclave, was converted into a mixture of diphenylstibine chloride (m. p. 68—70°) and phenylstibine dichloride (Morgan and Micklethwait, T., 1911, 39, 2295).

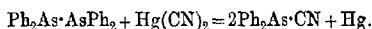
IV. Diphenylarsenious Cyanide.

(1) *From Diphenylarsenious Oxide.*—Diphenylarsenious oxide immersed in pure anhydrous hydrogen cyanide and left in contact with excess of this reagent for twenty-four hours yielded a yellow

oil which, on seeding with crystals of diphenylarsenious cyanide, solidified to a crystalline solid melting at 28—30° (Sturniolo and Bellinzoni, *Boll. chim. farm.*, 1919, **58**, 409, give m. p. 35°); this product contained 84 per cent. of diphenylarsenious cyanide and 12 per cent. of diphenylarsenious oxide. A similar experiment carried out with 90 per cent. hydrogen cyanide gave a product melting at 29—30°, and containing 87.5 per cent. of diphenylarsenious cyanide.

It was next found that it was quite unnecessary to work with anhydrous hydrogen cyanide in order to obtain diphenylarsenious cyanide. The following three methods, which are based on the use of cyanides of the heavy metals, rendered it possible to dispense entirely with concentrated aqueous solutions of hydrogen cyanide or its alkali salts.

(2) *From Diphenylcacodyl*.—Diphenylarsenious chloride (53 grams) was stirred at 100° with 30 c.c. of commercial hypophosphorous acid (30 per cent.). Diphenylcacodyl (tetraphenyldiarsine) separated in a yield of 83 per cent. This product was heated at 250° with mercuric cyanide in the rotating autoclave in the proportions demanded by the following equation:



The organic product was extracted with benzene, and the yield of diphenylarsenious cyanide was 94 per cent. of the calculated amount.

A similar experiment was carried out with silver cyanide, according to the equation



The result obtained was not so satisfactory.

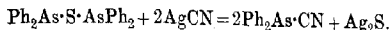
(3) *From Diphenylarsenious Sulphide*.—Diphenylarsenious chloride was dissolved in benzene and shaken for fifteen minutes with a saturated aqueous solution of sodium sulphide (1½ mols.). The benzene solution, washed with water, dried with anhydrous calcium chloride, and concentrated, yielded a mass of colourless needles of diphenylarsenious sulphide; yield, 93 per cent. After one recrystallisation, the substance melted at 64°.

The foregoing sulphide was mixed with mercuric cyanide in the following proportions and heated for two hours at 160—200°:



The organic product was separated from mercuric sulphide with dry benzene, the yield of diphenylarsenious cyanide being 71 per cent.

Experiments were also carried out, using silver cyanide, according to the equation



The temperature was kept at 160° and the product extracted with dry benzene as before, the yield of diphenylarsenious cyanide being 69 per cent.

(4) *From Diphenylarsenious Chloride.*—After preliminary experiments, the following method was adopted in the preparation of $7\frac{1}{2}$ kilos. of dry, alkali-free diphenylarsenious cyanide. Silver cyanide was prepared quantitatively from silver nitrate by precipitation with a dilute aqueous solution of hydrogen cyanide and dried at 120° .

Diphenylarsenious chloride was heated with a 10 per cent. excess of dry silver cyanide in the glass-lined rotating autoclave for three hours at 150 – 160° . The contents of the autoclave were allowed to cool to 40° , and filtered through a heated filtering apparatus. When the liquid had been thoroughly drained from the silver chloride, the latter was extracted with warm, dry benzene, and the clear solution distilled. The total yield of diphenylarsenious cyanide was about 92 per cent. of the calculated amount. The product, without further purification, melted at 28° , and contained 90 per cent. of the cyanide, the remaining 10 per cent. consisting of diphenylarsenious oxide and chloride.

In this operation, 5 kilos. of silver cyanide were employed, and, after washing with hot benzene until free from organic arsenicals, the residual silver chloride was reduced to silver by fusion with sodium carbonate. Even with an improvised smelting apparatus, the total loss of this metal was less than 2 per cent.

This paper is published with the consent of the Chemical Warfare Section of the War Office, to whom the authors tender their thanks for facilities accorded in the carrying out of this investigation.

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FINSBURY, LONDON, E.C.2.

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LXXXV.—*ortho*-Chlorodinitrotoluenes. Part I.

By GILBERT T. MORGAN and HARRY DUGALD KEITH DREW.

THE direct nitration of *o*-chlorotoluene as carried out by Nietzki and Rebe (*Ber.*, 1892, **25**, 3005) resulted in the isolation of one dinitro-compound, 2-chloro-3:5-dinitrotoluene. Further nitration of the 3- and 5-nitro-derivatives of *o*-chlorotoluene by Borsche and Fiedler led to the same dinitro-compound, these investigators indicating a melting point of 63–64°, whereas the earlier workers gave it as 45° (compare Rabaut, *Bull. Soc. chim.*, 1895, [iii], **13**, 634, and Körner and Contardi, *Atti R. Accad. Lincei*, 1915, [v], **24**, i, 888).

Another dinitro-compound (m. p. 106–107°) was obtained by Jansen (D.R.-P. 107505) on nitrating 2-chloro-6-nitrotoluene (compare Cohn, *Monatsh.*, 1901, **22**, 475).

In the research described below, the nitration of *o*-chlorotoluene to dinitro-derivatives has been investigated more completely, and two new isomerides are described and identified as the 4:5- and 4:6-dinitro-compounds.

Nitration of o-Chlorotoluene.

Eighty grams of *o*-chlorotoluene (I) were added during two hours to 400 c.c. of concentrated sulphuric acid and 180 c.c. of nitric acid (D 1.42) at 8–10°, the mixture being afterwards heated for four hours on the water-bath. The yellow, supernatant oil from three batches weighed 340 grams, and the spent acids, poured on to ice, gave an additional 36 grams (total yield, 91.5 per cent. of the theoretical).

The oily product partly solidified on cooling, and the solid portion, when crystallised from alcohol, yielded pure 2-chloro-3:5-dinitrotoluene (V); the alcoholic filtrate gave mixed crystals of this compound (m. p. 64°) and of the 5:6-isomeride (m. p. 101–106°). As a satisfactory separation of these two products could not be effected by alcohol, petroleum, benzene, or acetic acid, recourse was had to crystallisation from concentrated sulphuric acid, a method formerly employed by Crossley and Renouf in separating the dinitro-*o*-xylenes (*T.*, 1909, **95**, 202). The oily mixture (340 grams) was dissolved in 800 c.c. of concentrated sulphuric acid on the water-bath, and this solution yielded, on cooling, 43 grams of crystalline material, which, on fractional crystallisation from alcohol, gave 30 grams of the 5:6-dinitro-compound, 3 grams of the more soluble 4:5-isomeride (m. p. 87–88°), and 10 grams of an intimate mixture (m. p. 63–65°) of these two

isomeric compounds. The mixture contains the 4:5- and 5:6-isomerides in the proportions, respectively, of 2:1, and as this ratio represents their relative solubilities in alcohol, they are not readily separated from the mixture by the use of this solvent.

The concentrated acid filtrate, when treated with ice, gave 100 grams of crystals and 152 grams of oil. The solid part, when crystallised successively from concentrated sulphuric acid and alcohol, furnished a mixture of the 3:5- and 4:5-isomerides, the former predominating. The oily portion on similar treatment was fractionated chiefly into the same pair of isomerides and a small amount of the intimate mixture of the 4:5- and 5:6-isomerides.

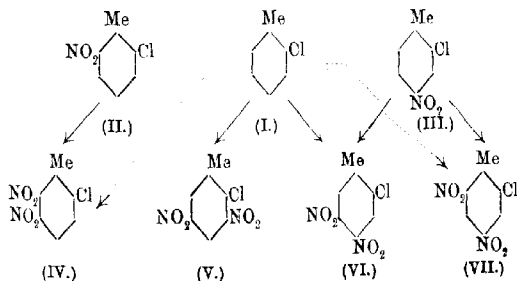
The process of crystallisation from concentrated sulphuric acid was repeated many times on the more fusible fractions melting below 50°. The two *o*-dinitro-compounds, the 4:5- and 5:6-isomerides, are less soluble in cold concentrated sulphuric acid than the *m*-dinitro-compounds, the 3:5- and 4:6-isomerides. Hence the former pair gradually accumulated in the crystalline fractions, whilst the latter became concentrated in the acid filtrate.

As the result of a lengthy, systematic fractionation, 340 grams of crude nitration product yielded 125 grams of the 3:5-dinitro-compound, 30 grams of the 5:6-isomeride, 15 grams of the 4:5-compound, and 63 grams of the intimate mixture (m. p. 63–65°) of the last two substances. The oily material obtained from the final filtrates, which consisted largely of impure 3:5-compound, gave the reactions of the 4:6-isomeride (m. p. 49°).

The 4:5- and 4:6-dinitro-compounds have been obtained more readily by the nitration of 2-chloro-4-nitrotoluene (p. 786), and further nitration of 2-chloro-6-nitrotoluene has given as the main product the 5:6-dinitro-compound (p. 787).

The solubilities in concentrated sulphuric acid or in methyl or ethyl alcohol of the three isomerides containing the nitro-groups in positions 3:5-, 4:5-, and 5:6- are respectively in the ratio 4:2:1.

The diagram below illustrates the derivation of the four



2-chlorodinitrotoluenes either directly from *o*-chlorotoluene or indirectly from 4- and 6-nitro-2-chlorotoluenes.

Nitration of 2-Chloro-4-nitrotoluene.

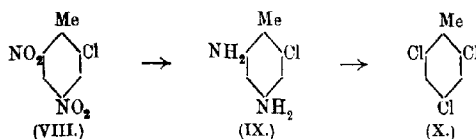
2-Chloro-4:5-dinitrotoluene (VI).—2-Chloro-4-nitrotoluene (III) (51 grams) was added slowly to 250 c.c. of concentrated sulphuric acid and 60 c.c. of nitric acid (D 1.42), the temperature being maintained at 40–45° for one hour. The mixture was then heated to 90° until the characteristic odour of the mononitro-compound had disappeared. When crystallised from alcohol, the nitration product yielded 49 grams of pure 2-chloro-4:5-dinitrotoluene melting at 88.5°, the yield being upwards of 85 per cent. (Found: Cl=16.58; N=13.15. $C_7H_5O_4N_2Cl$ requires Cl=16.37; N=12.93 per cent.).

2-Chloro-4:5-dinitrotoluene separated from cold alcohol in lustrous, colourless, hexagonal leaflets, or in tough, prismatic needles at higher temperatures.

2-Chloro-4:6-dinitrotoluene (VII).—The oily residue from the foregoing 4:5-dinitro-compound was subjected to fractional crystallisation from concentrated sulphuric acid in order to separate the other isomeride. The crystallising fraction consisted of nearly pure 4:5-dinitro-compound, whilst the acid filtrate yielded on dilution with water crystals of *2-chloro-4:6-dinitrotoluene* (m. p. 49°) and an oily mixture of the two isomerides. Repeated fractionation of this oil in concentrated sulphuric acid led to the gradual separation of the two constituents. The total yield of the 4:6-compound was about 12 per cent., of which half was isolated in a state of purity (Found: Cl=16.39; N=13.09. $C_7H_5O_4N_2Cl$ requires Cl=16.37; N=12.93 per cent.).

2-Chloro-4:6-dinitrotoluene is very soluble in alcohol, and crystallises in colourless, rectangular prisms or in prismatic needles. Like its isomerides, it is odourless. It does not react with aniline in boiling benzene, but with liquid or alcoholic ammonia it gives rise to ill-defined, shellac-like products.

With zinc dust, ammonium chloride, and dilute alcohol, or with alcoholic stannous chloride and hydrochloric acid, the 4:6-dinitro-compound underwent reduction to *6-chloro-2:4-tolylenediamine* (IX), crystallising from benzene or from alcohol and water in needles melting at 69.5°. With diazonium salts, this base gave the reactions of a meta-diamine; its constitution was determined by converting it, through the Sandmeyer reaction, into 2:4:6-trichlorotoluene (X), melting at 33–34° (Cohen and Dakin, T., 1902, 81, 1335).



Nitration of 2-Chloro-6-nitrotoluene.

2-Chloro-5:6-dinitrotoluene (IV).—A specimen of 6-nitro-*o*-toluidine, available through the kindness of Prof. Green, was converted by the Sandmeyer reaction into 2-chloro-6-nitrotoluene (II) (m. p. 36–37°), and the latter compound nitrated at 20° with 15 parts of concentrated sulphuric acid and 2 parts of nitric acid (D 1.42), the reaction being completed at 80°. The yield of 5:6-dinitro-compound was upwards of 85 per cent., and there was a small amount of oily by-product. 2-Chloro-5:6-dinitrotoluene melting at 106.5° separated from methyl or ethyl alcohol in colourless needles or prisms; its constitution was confirmed by the following processes.

Action of Ammonia on 2-Chloro-5:6-dinitrotoluene.—When treated either with liquefied ammonia or with saturated alcoholic ammonia, 2-chloro-5:6-dinitrotoluene was converted quantitatively into 6-chloro-3-nitro-*o*-toluidine, the inorganic product being ammonium nitrite entirely free from ammonium chloride. On crystallising from alcohol, the nitroamine separated in pale amber, highly refractive prisms with pyramidal ends; it melted at 151.5° and had a faint vanilla odour (Found: Cl=19.18; N=15.18. C₇H₇O₂N₂Cl requires Cl=19.01; N=15.02 per cent.).

*6-Chloro-3-nitro-*o*-toluidine* (XII), which was only very sparingly soluble in water, dissolved more readily in warm, moderately concentrated acid, ether, or the alcohols. It was not benzoylated under Schotten-Baumann conditions.

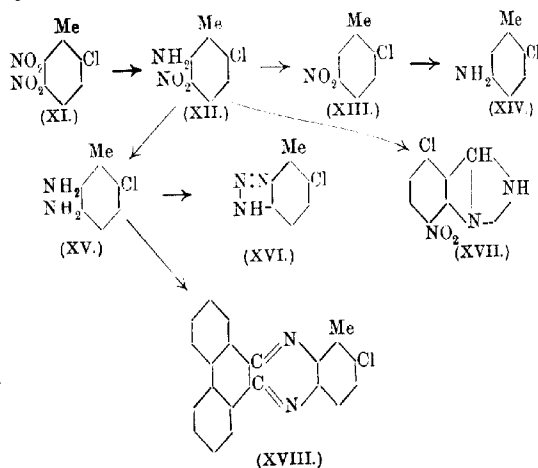
4-Chloro-7-nitroindazole (XVII).—A solution of the diazonium sulphate of the foregoing nitroamine (1.6 grams) was boiled with alcohol, and the product distilled in a current of steam, when the distillate contained 2-chloro-5-nitrotoluene (0.8 gram), and the residue yielded a voluminous mass of felted, yellow needles (0.6 gram), very sparingly soluble in hot water, crystallising from warm alcohol, and dissolving in aqueous sodium hydroxide to a bright yellow solution (Found: N=21.49; Cl=17.93. C₇H₄O₂N₃Cl requires N=21.28; Cl=17.95 per cent.). This indazole melted at 218°, and, on warming, had a marked odour resembling that of iodoform.

The foregoing 2-chloro-5-nitrotoluene (XIII) was characterised

by conversion into 6-chloro-*m*-toluidine (XIV) and its benzoyl derivative, these compounds melting respectively at 84° and 119–120° (Wibaut, *Rec. trav. chim.*, 1913, **32**, 244).

These results show that it is the 6-nitro-group which is displaced quantitatively by the amino-radicle. This displacement was unexpected, inasmuch as it was to be anticipated that the 5-nitro-group would be the most mobile of the three acidic substituents, owing to its position in regard to the chlorine atom and the other nitro-group. A similar case, in which, however, this anomalous displacement is not quantitative, has recently been described by Körner and Contardi (*Atti R. Accad. Lincei*, 1916, [v], **25**, ii, 339), who showed that 2:3:6-trinitrotoluene gave with alcoholic ammonia a mixture of 2:6-dinitro-*m*-toluidine and 3:6-dinitro-*o*-toluidine, the production of the latter base being another instance of the displacement of a nitro-group when contiguous to a methyl radicle (compare Kenner, T., 1914, **105**, 2717).

The orientation of the amino-group in 6-chloro-3-nitro-*o*-toluidine is demonstrated by the reactions summarised in the following diagram:



6-Chloro-2:3-tolylendiamine (XV), produced by reducing 6-chloro-3-nitro-*o*-toluidine with zinc dust and ammonium chloride in dilute alcohol, was obtained in the form of its hydrochloride (nacreous leaflets decomposing at 263°). The free base crystallised from benzene and light petroleum in colourless needles melting at 46–47°, and giving an *acetyl* derivative melting at

201–203°. The *diazimine* (XVI), precipitated by adding sodium nitrite to the dihydrochloride in dilute acetic acid, crystallised from hot chloroform or benzene in creamy-white, flocculent masses of minute plates melting at 232° (Found: N=25.52; Cl=21.30. $C_7H_6N_3Cl$ requires N=25.08; Cl=21.16 per cent.).

2-Chloro-1-methylbenzophenanthrazine (XVIII), prepared by heating 6-chloro-2:3-tolylenediamine and phenanthraquinone in glacial acetic acid, crystallised from benzene in woolly masses of yellowish-white needles melting at 244° (Found: Cl=10.75. $C_{21}H_{13}N_2Cl$ requires Cl=10.79 per cent.).

Action of Ammonia on 2-Chloro-4:5-dinitrotoluene.

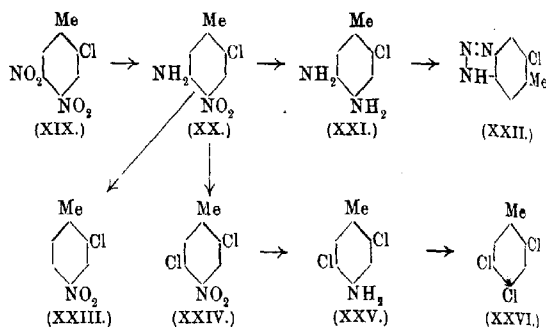
With liquid ammonia, the 4:5-dinitro-compound underwent far-reaching changes; ammonium nitrite and chloride were both produced, and the organic product was tarry and uncrystallisable. A simpler reaction occurred with saturated alcoholic ammonia, when 9 grams of the dinitro-compound yielded 8 grams of 6-chloro-4-nitro-*m*-toluidine (XX), a base crystallising from methyl alcohol in stout, brittle, orange-red prisms with pyramidal ends, or in orange-red, silky needles: both forms melted at 144°.* This amine is slightly volatile in steam, even in the presence of mineral acid; it has a faint odour of vanilla, and is readily soluble in organic solvents, although sparingly so in water (Found: Cl=19.18; N=15.23. $C_7H_7O_2N_2Cl$ requires Cl=19.01; N=15.02 per cent.).

The processes summarised in the diagram on p. 790 were carried out in order to determine the constitution of 2-chloro-4:5-dinitrotoluene and 6-chloro-4-nitro-*m*-toluidine.

(1) On boiling an alcoholic solution of 2-chloro-4-nitrotoluene-5-diazonium sulphate, 2-chloro-4-nitrotoluene (XXIII) (m. p. 65°) was obtained, volatile in steam and developing an intense red coloration with hot alcoholic sodium hydroxide.

(2) The diazonium chloride when treated by the Sandmeyer reaction yielded 2:5-dichloro-4-nitrotoluene (XXIV) (m. p. 47–50°), and this product on reduction gave 2:5-dichloro-*p*-toluidine (XXV), melting at 91–92° (Cohen, T., 1901, **79**, 1130; 1902, **81**, 1347). A repetition of the Sandmeyer reaction on this base furnished 2:4:5-trichlorotoluene (XXVI), melting at 82°.

* A nitroamine stated to have the same orientation as the foregoing preparation, which has been described as separating in yellowish-brown prisms melting at 158–159°, was prepared by nitrating 6-chloroaceto-*m*-toluidide and by subsequent hydrolysis. A by-product obtained simultaneously was described as 6-chloro-2-nitro-*m*-toluidine [(Badische Anilin- & Soda-Fabrik, D.R.-P. 226772).



(3) A similar diazo-solution, treated with excess of aqueous sodium carbonate and then added to an alkaline solution of resorcinol, gave a bright red azo-resorcinol, dyeing wood in orange-red shades not affected by after-chroming, which had evidently not lost the nitro-group.

6-Chloro-3:4-tolylendiamine (XXI).—The hydrochloride of this diamine was produced quantitatively by reducing 6-chloro-4-nitro-*m*-toluidine with zinc dust, ammonium chloride, and dilute alcohol, or with alcoholic stannous chloride. The free base crystallised in lustrous, pale brownish-yellow leaflets melting at 143° (Found: Cl=22.35; N=17.90. $C_7H_8N_2Cl$ requires Cl=22.64; N=17.89 per cent.).

The diazoimine (XXII), insoluble in water, crystallised from chloroform in pale flesh-coloured, woolly masses of minute needles melting at 192° (Found: Cl=21.37; N=25.33. $C_7H_6N_3Cl$ requires Cl=21.16; N=25.08 per cent.).

3-Chloro-2-methylbenzophenanthrazine, $C_{14}H_8 \begin{smallmatrix} N \\ \diagup \diagdown \\ N \end{smallmatrix} C_6H_2MeCl$, obtained by heating its generators in glacial acetic acid, separated from benzene in golden-yellow needles melting at $264-265^{\circ}$. Like its isomeride (p. 789), it developed an intense cerise coloration with concentrated sulphuric acid (Found: Cl=10.86. $C_{21}H_{13}N_3Cl$ requires Cl=10.79 per cent.).

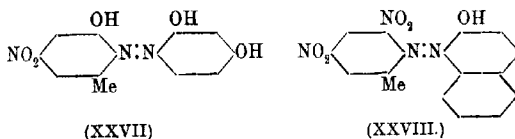
The Action of Ammonia on 2-Chloro-3:5-dinitrotoluene.

Dry ammonia gas passed to saturation into an alcoholic solution of 2-chloro-3:5-dinitrotoluene developed transient blue colorations, and then deposited 3:5-dinitro-*o*-toluidine (m. p. 213°), the yield being upwards of 95 per cent. Favourable results were obtained with methyl-alcoholic ammonia or with liquid ammonia. A similar

colour change was due to the formation of an additive compound with ammonia, since, on evaporating the violet solution in liquid ammonia, the residue consisted of unchanged 3:5-dinitro-compound, and was quite free from ammonium chloride or nitrite.

Azo-dyes from 3:5-Dinitro-o-toluidine.

3:5-Dinitro-*o*-toluidine* was diazotised either in concentrated sulphuric acid with solid sodium nitrite or by Witt's method, by adding a mixture in molecular proportions of the base and potassium metabisulphite to fuming nitric acid at -5° to 0° . The diluted diazo-solutions were neutralised by pouring into 3 per cent. aqueous sodium carbonate at 0° . A yellow, amorphous substance was deposited, the yield being about 30 per cent. of the base taken. The bright yellow filtrate, which contained a very stable diazo-compound, was added to an alkaline solution of resorcinol; the liquid was then heated on the water-bath, and sodium chloride was added to precipitate the alkali salt of the *azo*-dye. The free hydroxyazo-derivative (XXVII) separated from ether in lustrous,



crimson crystals decomposing at $256-257^{\circ}$ (Found: $N=14.10$. $C_{13}H_{11}O_5N_3$ requires $N=14.53$ per cent.).

The *triacetyl* derivative of this hydroxyazo-dye, obtained by adding a trace of concentrated sulphuric acid to a suspension of the dye in acetic anhydride, crystallised from dilute acetic acid or alcohol in pale red needles melting at $147-148^{\circ}$ (Found: $N=10.38$. $C_{19}H_{17}O_8N_3$ requires $N=10.12$ per cent.).

Further confirmation of the formula (XXVII) ascribed to the azo-resorcinol derivative was obtained by the fact that it dyed wool from an acid bath in orange-red shades, which were changed to dark purple tints by conversion into the chrome lake of the dye either by after-chroming or by the metachrome process.

3:5-Dinitrotoluene-2-azo- β -naphthol (XXVIII), produced by adding the dilute acid solution of 3:5-dinitrotoluene-2-diazonium sulphate to alkaline β -naphthol, crystallised from glacial acetic acid in lustrous, dark crimson needles melting at 226° (Found: $N=16.53$. $C_{17}H_{12}O_5N_4$ requires $N=15.90$ per cent.).

* This dinitro-base and the amines XII and XX (pp. 787 and 789) gave the Green and Rowe test for *o*- and *p*-nitroamines (T., 1913, 103, 508).

Colour Reactions of the 2-Chlorodinitrotoluenes.

The following colour changes were found useful in identifying the four isomeric 2-chlorodinitrotoluenes:

Isomeride.	Anhydrous liquid ammonia (the gas liquefied on to the solid).	Alcoholic ammonia (gas passed into alcoholic solution).	Alcoholic sodium hydroxide.
1. 3:5- (m. p. 64.5°).	Intense violet to bluish-violet (red by transmitted light), changing to greenish-black.	Greenish to azure-blue, changing to red (tr.).	Pale yellow (tr.) to greenish-blue, to intense rose-red. On heating to bright orange-red (tr.).
2. 5:6- (m. p. 106.5°).	Yellow (tr.) to orange-red (tr.)	Yellow (tr.).	Faint yellow (tr.). On heating to orange, to deep orange-red, fading to brownish-yellow (tr.), finally light orange (tr.).
3. 4:5- (m. p. 88.5°).	Orange-red (tr.) to bluish- and brownish-black.	Orange-red (tr.).	Pale yellow (tr.) to intense emerald-green, to blue, bluish-black to brownish-red. On heating to pale orange-red (tr.).
4. 4:6- (m. p. 49°).	Intense violet to bluish-violet, to magenta and finally deep crimson.	Bright red (tr.) to bluish-green, to intense azure-blue (red by transmitted light), to deep crimson.	Intense blue to greenish-blue, to brownish-black. On heating to reddish-black, and finally to deep orange-red (tr.).

In all cases, the colorations were opaque unless marked "tr." = transparent. Intense violet and blue colorations with anhydrous and alcoholic ammonia were obtained with both meta-dinitro-compounds, whereas the two ortho-dinitro-isomerides gave orange-red tints.

Summary.

(1) The nitration of *o*-chlorotoluene in mixed nitric-sulphuric acid leads to a mixture of isomeric dinitro-compounds (90 per cent. of the calculated amount). The loss is occasioned by oxida-

tion and sulphonation. The nitration mixture contains four isomerides in approximately the following percentage amounts:

				Per cent.
3:5-Dinitro-2-chlorotoluene	55—60
5:6- " "	18—20
4:5- " "	18—20
4:6- " "	1—2

(2) The existence of the four isomeric dinitro-2-chlorotoluenes in the nitration mixture shows that the orientation due to methyl is not entirely overpowered by that of the more actively directive chlorine substituent. The influence of the methyl group is more powerful in the first stage of nitration, when it accounts for 38 per cent. of the mono-nitrated products (Wibaut, *loc. cit.*), whereas in the second stage of the process its effect accounts for less than 10 per cent. of the final product.

(3) Nitration of 2-chloro-6-nitrotoluene leads to the formation of 2-chloro-5:6-dinitrotoluene as main product, the yield of this isomeride being about 90 per cent.

(4) Nitration of 2-chloro-4-nitrotoluene gives 2-chloro-4:5-dinitrotoluene as main product (upwards of 85 per cent.) and 2-chloro-4:6-dinitrotoluene as by-product (yield about 12 per cent.).

(5) These dinitro-2-chlorotoluenes contain labile acid radicles displaceable by amino-groups. In this reaction, addition of ammonia to the aromatic compound precedes substitution, the first phase in the reaction being accompanied by the development of intense colorations.

The authors desire to express their thanks to the Advisory Council for Scientific and Industrial Research for grants which have partly defrayed the expenses of this investigation.

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LXXXVI — *The Oxidation of the Ingredients of Banded Bituminous Coal. Studies in the Composition of Coal.*

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It has been shown that the four macroscopically distinct portions, vitrain, clarain, durain, and fusain, into which banded bituminous coal can be separated differ in essential microscopical structure (Stopes, *Proc. Roy. Soc.*, 1919, [B], **90**, 470), in their behaviour towards reagents and on destructive distillation (Tideswell and Wheeler, T., 1919, **115**, 619), in their behaviour on coking, and in the composition of their mineral constituents (Lessing, this vol., pp. 247, 256). The differences in chemical constitution between the ingredients disclosed by a decrease in their reactivity towards solvents, reagents, and heat-treatment (in the order vitrain, clarain, durain), seem to be due to a variation in the proportions in which the constituents of the coal conglomerate are present in each ingredient of the banded coal rather than to the presence in any one of them of fundamentally distinct types of compounds. Fusain, which is much less reactive in most respects than the remainder of the coal substance, requires separate consideration.

In view of their known differences, the separate ingredients of banded coal are more suitable materials for the study of the oxidation of "coal" in relation to its spontaneous combustion than are bulk samples. For it is clear that lumps of banded coal, although obtained by careful quartering of the bulk samples, may differ markedly one from another, in chemical composition and general properties, dependent on the distribution of the different bands in them.

Samples of the four ingredients from the Hamstead Thick Coal have been subjected to the action of air or oxygen at different temperatures to determine their rates of oxidation and relative ignition-temperatures. The experiments were designed to yield, in addition to information as to the comparative behaviour of the four ingredients of banded coal, data which would be of service to the general research on the mechanism of the reaction between oxygen and the coal conglomerate on which we are engaged.

Relative Ignition-temperatures.

The method of experiment has been described in T., 1918, 113, 949, which should be consulted. Insufficient fusain was available for the determination: the other ingredients did not show any marked differences in their relative ignition-temperatures as judged by the points of intersection of the time-temperature curves. The tests were carried out under identical conditions as regards rate of heating, speed of passage of air-current, etc., and the "ignition-temperatures" recorded ranged from 170° to 175° for each ingredient.

It was clear, however, from the difference in slope of the heating-curves for the coals compared with that for the sand-bath, that the wide differences in the amounts of moisture contained in the three ingredients affected in a different degree in each instance the rate of rise of temperature of the coal due to oxidation. The moisture-content chiefly determines the lag at low temperatures (up to 80°) between the temperature of the coal and that of the sand-bath, and this lag affects the point of intersection of the two curves. Consideration of the rates of heating of the coals at temperatures above 80° (at which temperature nearly all moisture had been driven off) indicated that vitrain and clarain were almost equally liable to self-heat, whilst durain appeared appreciably less liable.

Rate of Absorption of Oxygen.

The apparatus employed, constructed wholly of glass without rubber connexions, enabled a continuous stream of air or oxygen to be circulated through the sample of coal to be tested, which was contained in a horizontal reaction-tube, 1.5 cm. in diameter, maintained at the experimental temperature by means of an electrically heated air-oven. Suitable stop-cocks in the circuit enabled the reaction-tube to be by-passed, or to be exhausted separately from the rest of the apparatus. A by-passed calcium chloride tube, for drying the gases, was included in the circuit.

Twenty grams of the coal, undried and broken into pieces capable of passing through a 10×10 and remaining on a 60×60 mesh sieve, were packed tightly in the reaction-tube and held in position by plugs of glass-wool. The coal was then exhausted during forty-eight hours at the ordinary temperature, and finally at 200°, the gases removed (original occluded gases) being collected and analysed. In the meantime, the remainder of the apparatus (the volume of which could be adjusted to be 1100, 2100, or

3100 c.c. as required) had been filled with oxygen at rather more than atmospheric pressure, and circulation begun, through the by-pass of the reaction-tube, by means of an automatic mercury pump.

The coal having been brought to the experimental temperature, the reaction-tube was included in the circuit, which formed a closed system, and readings of the gas pressure were at once taken. Thereafter, readings of the temperature, gas pressure, and barometer were taken at frequent intervals during 120 hours, the rate of circulation of the oxygen through the coal being maintained at 1 litre per hour.

At the end of the circulation period of each experiment (which yielded time-pressure curves, from which the rate of absorption of oxygen by the coal could be calculated), the coal was rapidly cooled to the ordinary temperature, and the gases remaining in the reaction tube were removed by exhaustion during several hours and transferred to the main part of the apparatus. The temperature of the coal was then raised to 200°, and the gases obtained by exhaustion during twenty-four hours were collected separately and analysed. A sample of the oxygen (containing carbon dioxide and carbon monoxide) in the main part of the apparatus was also taken. After allowing the reaction-tube to cool to the temperature required for the next experiment, fresh oxygen was introduced into the apparatus, and the cycle of operations repeated. In the series of oxidations of vitrain, clarain, and durain, the temperatures were 15°, 50°, 100°, 50°, and 50°; with fusain the order was 50°, 50°, 15°, 100°, and 50°.

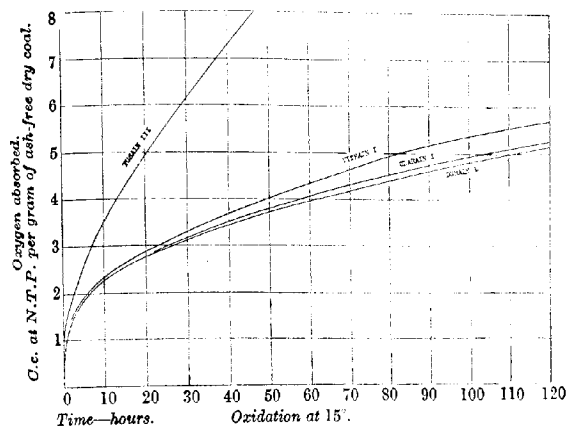
In Figs. 1, 2, and 3, curves are given showing the relation between time and the volume of oxygen absorbed by each of the ingredients of the banded Hamstead coal at 15°, 50°, and 100°. The series of oxidations at the three temperatures were made with each ingredient on the same sample, which was not removed from the absorption apparatus until the series relating to it was completed. Before each oxidation at a given temperature, the coal, in position in the absorption apparatus, was exhausted at 200°, as already described, until gases ceased to be evolved.

It has been shown (T., 1918, 113, 949; 1919, 115, 895) that, in a manner analogous to the burning of carbon, the immediate result of the absorption of oxygen by coal may be considered to be the formation of a coal-oxygen complex. This complex on being raised slightly in temperature decomposes, evolving carbon dioxide, carbon monoxide, and water, and leaving a residue but little altered in character from the original coal.

Preliminary experiments had shown that it was possible to heat

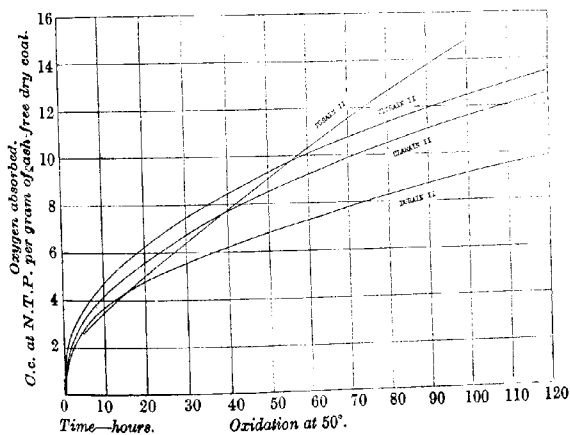
the Hamstead coal "saturated" with oxygen to a temperature as high as 200°, and to exhaust it at that temperature, without

FIG. 1.



materially altering the composition of the coal substance or producing any effects other than to decompose the coal-oxygen complex

FIG. 2.

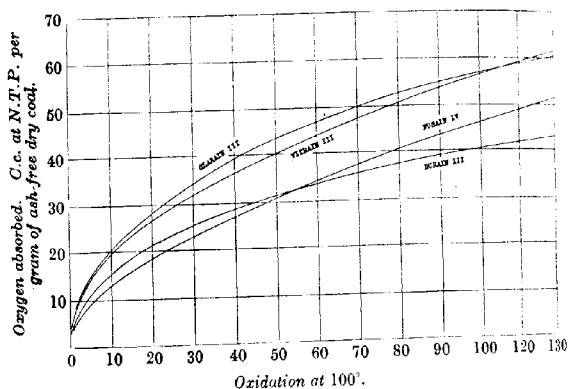


and to remove small quantities of gaseous paraffin hydrocarbons (the higher members of the series). The proportion of the complex

that decomposes into the simple oxides increases rapidly with increased temperature; hence the necessity for exhausting the "saturated" coal at as high a temperature as possible. By such exhaustion, the coal recovers to a great extent its capacity for absorbing oxygen—that is to say, its capacity for complex-formation—the recovery amounting to about 95 per cent. of the original capacity after exhaustion at 200° . It may be noted that the Hamstead coal is particularly adapted to experiments of this nature by reason of the small quantities of occluded paraffins that it contains.

A study of the absorption curves discloses differences between the three ingredients, vitrain, clarain, and durain, of the same order

FIG. 3.



as might be anticipated from their differences in composition. All three absorb oxygen to a marked degree, but there is a decrease in absorptive power in the order vitrain, clarain, durain which is particularly marked at low temperatures (15°). At higher temperatures (50°), the difference between vitrain and clarain decreases, and at 100° the absorptive power of each is nearly the same. It is possible that at still higher temperatures clarain would take the lead. Durain, throughout the series of experiments, displayed less absorptive power than either vitrain or clarain, the absorption of oxygen by durain being 10 per cent. less than by vitrain at 15° and 30 per cent. less at 100° .

The temperature-coefficients of the reactions (K_{10}), calculated from the total absorptions during 120 hours, are:

Temperature range :	Vitrain.	Clarain.	Durain.	Fusain.
15—50°	1.301	1.298	1.217	1.538
50—100°	1.407	1.414	1.387	1.013
Mean value over :				
15—100°	1.362	1.365	1.313	1.203

Fusain stands apart from the rest of the coal, as in its chemical properties generally, in its high absorptive power at low temperatures, and its low temperature-coefficient. At 100°, fusain absorbs oxygen scarcely more readily than does durain.

The ease of oxidation of the four ingredients of Hamstead coal should be compared with their power of absorbing moisture and the halogens:

	Vitrain.	Clarain.	Durain.	Fusain.
Moisture-content, per cent.	12.40	11.95	7.00	4.30
Absorption of iodine, per cent.				
(a) Aqueous, in 24 hours	33.5	34.0	26.6	6.4
(b) Wijs' solution, in 6 hours	86.5	84.0	68.4	12.8
Absorption of oxygen, c.c. per gram.				
At 100° in 120 hours	60.9	60.3	43.2	51.6

Whilst the absorption of oxygen and the halogens by coal is certainly not entirely a physical phenomenon, the magnitude of the effect for a coal of given composition may well be proportional to the concentration of the oxygen or the halogens maintained within it by purely physical absorption. In this connexion, the observation by Winmill (*Trans. Inst. Min. Eng.*, 1916, **51**, 494) may be cited, that the rate of absorption of oxygen by coal varies approximately as the square root of the partial pressure of the oxygen. Such a relationship would be expected were the amount of oxygen entering into chemical combination in a given time with the coal substance dependent on the concentration of oxygen within the coal.

Judged from this point of view, the difference in absorptive power evinced by the three ingredients, vitrain, clarain, and durain, would lie in their physical structure—in their power of physical absorption. This does not necessarily imply that the subsequent chemical action, or the products of such action, are identical in each instance, although there is undoubtedly a great similarity between them.

The data obtained by the exhaustion of the oxidised coals at 200° throws some light on this matter. The main facts elicited from a study of the quantities and compositions of the gases thus obtained (see tables I and II) are:

(1) There is a rapid and continuous increase in the amount of gas evolved (that is to say, in the amount of decomposition of the coal-oxygen complex) as the temperature of exhaustion of the coal after oxidation is increased.

TABLE I.
Gases Evolved on Exhaustion.

Temperature during exhaustion.	A.		B.	
	From durain, after oxidation at 100°. C.c.		From same sample of durain (after experiment A), after oxidation at 50°. C.c.	
	CO ₂ .	CO.	CO ₂ .	CO.
15—100°	2.7	0.7	3.1	0.8
100—150°	18.5	5.2	4.5	1.6
150—200°	63.8	15.1	15.8	4.5

TABLE II.

	Series Number.	Temperature of oxidation.	Vitrain.	Clarain.	Durain.	Fusain.
Oxygen absorbed. C.c. per gram of ash-free dry coal.	I.	15°	5.7	5.2	5.15	12.63
	II.	50	13.4	12.5	9.9	45.0
	III.	100	60.9	60.3	43.2	51.6
	IV.	50	9.2	9.5	7.0	15.0
	V.	50	8.8	8.3	5.9	10.0
Carbon dioxide evolved on exhaustion at 200°.	Original occluded gases.		1.61	1.30	0.90	1.06
	I.	15	0.59	0.60	0.49	0.32
	II.	50	1.71	1.38	1.13	0.77
	III.	100	6.85	6.40	4.79	4.55
	IV.	50	3.28	2.20	1.91	—
	V.	50	2.68	1.60	1.80	1.29
Carbon monoxide evolved on exhaustion at 200°.	Original occluded gases.		0.30	0.26	0.16	0.25
	I.	15	0.16	0.17	0.13	0.10
	II.	50	0.48	0.40	0.30	0.27
	III.	100	1.65	1.60	1.19	1.29
	IV.	50	0.72	0.67	0.51	—
	V.	50	0.58	0.47	0.45	0.38
Ratio CO ₂ /CO evolved on exhaustion at 200°.	Original occluded gases.		5.35	5.08	5.50	4.10
	I.	15	3.64	3.60	3.73	3.10
	II.	50	3.54	3.44	3.74	2.95
	III.	100	4.57	3.99	4.00	3.52
	IV.	50	4.54	3.40	3.73	—
	V.	50	4.62	3.40	4.06	3.40

(2) The amount of complex formed, as judged by the volumes of carbon dioxide and carbon monoxide subsequently evolved on exhaustion at 200°, increases rapidly with the temperature of oxidation.

(3) There is a variation in the amount of decomposition of the complex dependent on the previous treatment to which the coal has been subjected. This was most marked after the coal had been

oxidised at 100° and exhausted at 200°. Before this treatment, oxidation at 50° (Series No. II) and exhaustion at 200° released as carbon dioxide and carbon monoxide 12 per cent. of the oxygen absorbed at 50°; subsequently (Series Nos. IV and V), 40 per cent. was so released.

(4) There is a difference between the four ingredients as regards the ease of decomposition of the complex, the proportion of the absorbed oxygen released as carbon dioxide and carbon monoxide being considerably less with clarain than with vitrain or durain (except after oxidation at 15°). This suggests that the chemical reaction which follows the physical absorption of oxygen, and is responsible for its final disappearance, varies somewhat in degree, and perhaps also in nature, as between one ingredient of the banded coal and another. With fusain, the oxygen complex is either formed to a less extent than with the other parts of the coal, or, when formed, is more difficult to decompose.

The general conclusions to be drawn from the experiments as regards the banded bituminous coal are:

(1) Of the three main ingredients of the banded coal, the bright ones, vitrain and clarain, show greater liability to oxidise and to ignite than the dull durain. The difference between these ingredients is not, however, so great as to warrant any suggestion that the bright portions of Hamstead coal are primarily responsible for its liability to spontaneous combustion.

(2) The influence of fusain is uncertain. Many practical miners consider that spontaneous combustion originates where "mother-of-coal" (fusain) abounds. The results of our experiments lead us to consider it improbable that fusain has a preponderating influence in determining the actual ignition of the coal after self-heating has begun; but it is conceivable that the rapid absorption of oxygen by fusain at low temperatures may be attended by a sufficient evolution of heat to raise appreciably the temperature of the main mass of the coal, thereby causing the most inflammable ingredient (vitrain) to react more readily with oxygen.

To determine this matter with certainty, and it is clearly one which demands settlement, further experiments with a number of samples of fusain from different coals are required. We are addressing ourselves to this problem as being part of the general study of the oxidation of coal.

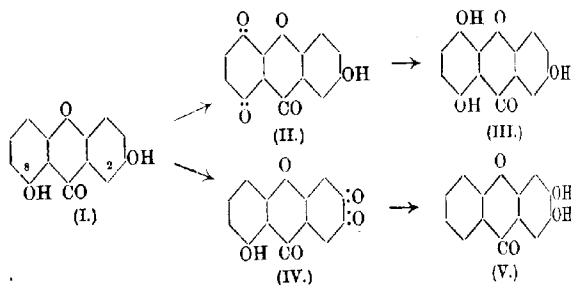
HOME OFFICE EXPERIMENTAL STATION,
ESKMEALS.

[Received, May 18th, 1920.]

LXXXVII.—8-Hydroxy-2:3-quinoxanthone.

By HARRY FITZGIBBON DEAN and MAXIMILIAN NIERENSTEIN.

WHEN euxanthone (I) is oxidised with chromic acid, a red product is formed, to which the formula 2-hydroxy-5:8-quinoxanthone (II) has been assigned (Nierenstein, *Ber.*, 1913, **46**, 649). On reduction, this substance yields the corresponding pale yellow 2:5:8-trihydroxyxanthone (III). Van Scherpenberg (*Diss.*, Delft, 1918, 68; *Chem. Weekblad*, 1919, **16**, 1146) has pointed out that since the quinoxanthone gives trinitroresorcinol on treatment with nitric acid, its probable constitution is 8-hydroxy-2:3-quinoxanthone (IV), the reduction product being the corresponding 2:3:8-trihydroxyxanthone (V). These contentions of van Scherpenberg are in the best agreement with the results given in the present communication.



EXPERIMENTAL.

The original method for the oxidation of euxanthone was found, as previously stated (*loc. cit.*), to give a product which crystallised only with difficulty. This may be overcome by using the following modification: To a well-cooled solution of 5 grams of euxanthone in 75 c.c. of glacial acetic acid, 10 grams of chromic acid dissolved in 150 c.c. of glacial acetic acid, also well cooled, are slowly added during three hours. The mixture is kept on ice for twenty-four hours, water is then added, and the precipitate crystallised from glacial acetic acid. This product gives all the colour reactions previously described. The average yield is 70 per

cent. of the theoretical (Found: C=64.5; H=2.7. Calc.: C=64.5; H=2.5 per cent.). Preparations which may be readily crystallised are also obtained when 2:3:8-trihydroxyxanthone (V) is oxidised with *p*-benzoquinone (A. G. Perkin, T., 1913, 103, 657). A solution of 1 gram of the trihydroxyxanthone in 25 c.c. of absolute alcohol is treated in the cold with 0.5 gram of *p*-benzoquinone, and the solid formed is crystallised from glacial acetic acid. The average yield is 73 per cent. of the theoretical (Found: C=64.3; H=2.6. Calc.: C=64.5; H=2.5 per cent.).

On heating molecular proportions of the quinoxanthone (prepared by the original or by either of the above-given methods) with 3:4-tolylenediamine in glacial acetic acid solution, the corresponding *azine* is easily obtained, which conclusively proves the ortho-quinonoidal structure of the compound. The azine crystallises from glacial acetic acid in deep red needles, which darken and subsequently char between 328° and 340° without melting (Found: N=8.3, 8.7. $C_{20}H_{14}O_3N_2$ requires N=8.5 per cent.).

2:3-Methylenedioxy-8-methoxyxanthone.

As in the case of isoquercetone (Nierenstein, T., 1915, 107, 870), an excess of diazomethane converts the quinone into the above-mentioned derivative. The reaction is carried out in ethereal suspension, the theoretical yield being obtained. The substance crystallises from alcohol in colourless needles, which melt and decompose at 211–212° (Found: C=66.5; H=3.8; OMe=11.0. $C_{15}H_{10}O_5$ requires C=66.7; H=3.7; OMe=11.5 per cent.).

2:3-Dihydroxy-8-methoxyxanthone.

This substance is obtained on removing the methylene group by Fittig and Remsen's method (*Annalen*, 1873, 168, 97), the technique being the same as in the case of the corresponding isoquercetone derivative (*loc. cit.*). It crystallises from alcohol in colourless needles, which melt and decompose at 249–251°. The alcoholic solution gives a green colour with alcoholic ferric chloride. It dyes calico mordanted with aluminium faintly, thus resembling 2:3-dihydroxyxanthone (Liebmann and Lindenbaum, *Ber.*, 1904, 37, 2736) (Found: C=64.8; H=4.2. $C_{14}H_{10}O_5$ requires C=65.1; H=3.9 per cent.).

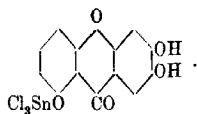
2:3:8-Trimethoxyxanthone.

This derivative is prepared from the previously-mentioned dihydroxy-compound by the action of methyl sulphate. It

crystallises from alcohol in faintly yellow needles, which melt at 194–195°. This substance is identical with that formerly described as 2:5:8-trimethoxyxanthone, which was prepared by the action of diazomethane on the corresponding trihydroxyxanthone.

2:3-Diacetoxy-8-methoxyxanthone, prepared by digesting the dihydroxy-compound with acetic anhydride and anhydrous sodium acetate, crystallises from alcohol in colourless needles, which melt and decompose at 231–232° (Found: C=63.0; H=4.3. $C_{18}H_{14}O_6$; requires C=63.2; H=4.1 per cent.).

The relative positions of the hydroxyl groups in 2:3:8-trihydroxyxanthone (V) become still more evident on comparison with euxanthone (I). (1) 2:3:8-Trihydroxyxanthone, on treatment with methyl sulphate ($3\frac{1}{2}$ mols.), is not fully methylated, the hydroxyl group in position 8 not being attacked, as in the case of euxanthone (v. Kostanecki, *Ber.*, 1894, **27**, 1992; Herzig and Klimosch, *ibid.*, 1908, **41**, 3894; compare, however, A. G. Perkin, *T.*, 1913, **103**, 1632, who finds that under certain conditions alkylation of this type of hydroxyl group may take place). (2) The resulting 8-hydroxy-2:3-dimethoxyxanthone is coloured, forms yellow solutions with alkalis, and possesses tinctorial properties similar to 8-hydroxy-2-methoxyxanthone (Herzig and Klimosch, *loc. cit.*; compare also Perkin and Everest, "The Natural Organic Colouring Matters," p. 125). (3) Like euxanthone (Pfeiffer, *Ber.*, 1911, **44**, 2653; compare also Herzig and Schönbach, *Monatsh.*, 1912, **33**, 673), 2:3:8-trihydroxyxanthone reacts with stannic chloride, forming the compound,



The corresponding tin compound is also obtained from 8-hydroxy-2:3-dimethoxyxanthone. 2:3-Dihydroxy-8-methoxyxanthone gives quite unexpectedly the same substitution product as 2:3:8-trihydroxyxanthone.

2:3:8-Trihydroxyxanthone differs, however, in one way from euxanthone. It has been shown (Herzig, *Monatsh.*, 1891, **12**, 161; 1897, **18**, 700; Herzig and Klimosch, *ibid.*, 1909, **30**, 527) that when euxanthone is methylated with diazomethane, 2-hydroxy-8-methoxyxanthone is formed, the 2-hydroxy-group not being susceptible to any form of methylation. This is not the case when 2:3:8-trihydroxyxanthone is methylated with diazomethane, all

three hydroxy-groups behaving in a similar manner, as previously shown (*loc. cit.*). Also 2:3-dihydroxy-8-methoxyxanthone, when methylated with methyl sulphate, yields the trimethoxy-derivative, as described above.

8-Hydroxy-2:3-dimethoxyxanthone, prepared by the action of methyl sulphate ($3\frac{1}{2}$ mols.) on an alcoholic solution of the trihydroxyxanthone, crystallises from alcohol in faintly yellow needles, which melt and decompose at $228-231^{\circ}$. It dissolves in dilute sodium hydroxide with a yellow colour, and dyes calico mordanted with aluminium faintly. Diazomethane converts it quantitatively into the corresponding trimethoxyxanthone (m. p. 195°) (Found: C=66.0; H=4.7; OMe=22.8. $C_{15}H_{12}O_5$ requires C=66.2; H=4.4; OMe=22.8 per cent.).

8-Acetoxy-2:3-dimethoxyxanthone, prepared in the usual manner, crystallises from alcohol in colourless needles, which melt and decompose at $224-225^{\circ}$ (Found: C=65.2; H=4.7. $C_{17}H_{14}O_6$ requires C=65.0; H=4.4 per cent.).

Action of Stannic Chloride on 2:3:8-Trihydroxyxanthone.

One gram of the trihydroxyxanthone dissolved in 75 c.c. of *s*-tetrachloroethane was heated with 2 grams of stannic chloride dissolved in 50 c.c. of the same solvent. The solution was kept at the boiling point for two hours, and the solid collected and washed, at first with *s*-tetrachloroethane and subsequently with benzene. Great care was taken to avoid the presence of moisture. The product was crystallised from *s*-tetrachloroethane, from which it separated in deep red crystals. These did not melt below 330° , but darkened at about $285-290^{\circ}$. When dissolved in boiling pyridine, a red solution with a blue fluorescence is obtained. The compound is slowly decomposed by water at the ordinary temperature; boiling greatly accelerates the decomposition. The analysis of this substance and of the other tin compounds was carried out according to the methods given by Pfeiffer (*Annalen*, 1910, **376**, 344) (Found: Cl = 22.2; Sn = 25.5. $C_{13}H_7O_3Cl_3Sn$ requires Cl=22.7; Sn=25.4 per cent.).

Action of Stannic Chloride on 8-Hydroxy-2:3-dimethoxyxanthone.

Five grams of the substance dissolved in benzene were heated with 4 grams of stannic chloride in 50 c.c. of benzene for two hours. The product was collected, washed with dry benzene, and thoroughly dried in a vacuum over phosphoric oxide. The substance dissolves in pyridine with a pale orange colour; it is insoluble in alcohol or benzene. Water decomposes it on keeping

and on boiling. The substance has no definite melting point, decomposing at about 311—325°. The yield was 7.8 grams (Found: Cl=21.6, 21.2; Sn=24.8, 24.6. $C_{15}H_{11}O_5Cl_3Sn$ requires Cl=21.4; Sn=24.0 per cent.).

Action of Stannic Chloride on 2:3-Dihydroxy-8-methoxyxanthone.

When 1 gram of the monomethoxy-derivative dissolved in 50 c.c. of *s*-tetrachloroethane is heated with 1 gram of stannic chloride in 50 c.c. of the same solvent, no precipitate is at first formed. After three-quarters of an hour's heating, the substitution product commences to appear, the reaction being completed in six hours. So far as it is possible to judge, the product is identical with that formed when 2:3:8-trihydroxyxanthone reacts with stannic chloride. For the analyses, two different preparations were used (Found: Cl=22.6, 22.9; Sn=25.9, 25.7. Calc.: Cl=22.7; Sn=25.4 per cent.).

In view of these results, the compound previously described (*loc. cit.*) as 2:5:8-triacetoxyxanthone is now considered to be 2:3:8-triacetoxyxanthone.

We are indebted to the Colston Society of the University of Bristol for a grant which has covered the expenses of this research.

BIO-CHEMICAL LABORATORY, CHEMICAL DEPARTMENT,
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[Received, June 1st, 1920.]

LXXXVIII.—*The Decomposition of Nitric Esters.*

By ROBERT CROSBIE FARMER.

IN a recent paper on the decomposition of nitric esters by lime (this vol., p. 552), Lowry, Browning, and Farmery have expressed the view that the primary decomposition of nitric esters is not a hydrolysis, but a decomposition to aldehyde (Berthelot), possibly through an alcohol peroxide (Klason and Carlson). Their grounds for this belief are the almost complete absence of glycerol in the products of decomposition of glyceryl trinitrate (and of the corresponding alcohols in other cases) and the fact that this formula-tion would give, as the primary decomposition product of glyceryl trinitrate, the dialdehyde, $CHO \cdot CO \cdot CHO$, which would conveniently account for many of the products which are actually

found to result. This mechanism of the decomposition of glyceryl trinitrate was previously suggested by Berl and Delpy (*Ber.*, 1910, 43, 1421), who regarded it, however, as a secondary reaction preceded by a hydrolysis. The latter view is so strongly supported by experimental evidence that Lowry, Browning, and Farmery's criticism of the views of Silberrad and Farmer (*T.*, 1906, 89, 1759) cannot be upheld.

From the nature of the hydroxy-acids, etc., isolated by Silberrad and Farmer (*T.*, 1906, 89, 1182) and others, the intermediate formation of the above aldehyde, although hypothetical, is readily conceivable. It does not, however, by any means follow that such aldehydes represent the initial stage of the decomposition. If we go back to first principles, it is clear that the nitric group has oxygen to spare, whilst the carbon nucleus is ready to take up oxygen. When hydrolytic agents are added (acid or alkali), the structure is loosened, in accordance with the general behaviour of esters; at the moment of splitting, however, the carbon nucleus is in a condition so sensitive to oxidation that the alcohol and acid are not actually formed, or are formed only to a minor extent. This was clearly brought out by Silberrad and Farmer, who showed that, if once formed as complete molecules, they do not interact at the dilutions in question (although, as is well known, glycerol can be oxidised to aldehydes and ketones by nitric acid under suitable conditions). The acid and alcohol groups must react, therefore, with the formation of oxidation products of the alcohol. This is tantamount to saying that the nitric acid in the moment of its formation oxidises the carbon nucleus. Beyond this, the rest of the process may well proceed as indicated by Lowry, Browning, and Farmery.

The primary hydrolysis is in accordance with the universal behaviour of esters, and it would require much more than speculative evidence to justify the view that nitric esters form an exception to the general rule. If some other form of primary decomposition did occur, it would at least appear inevitable that hydrolysis should take place concurrently, and thus we are driven in any case to the conclusion that the nitric acid in the moment of formation oxidises the alcohol nucleus whenever the alcohol is not found as a product of the reaction.

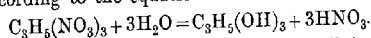
Regeneration of Alcohols from Nitric Esters.

The basis of the argument against hydrolysis is that the alcohol is not ordinarily found as a product of the decomposition. In view of this, it is somewhat surprising that Lowry, Browning, and Farmery claim to have shown that nitrocellulose breaks down in

successive stages to cellulose trinitrate and dinitrate, for this would clearly imply that a normal hydrolysis of a nitric ester group can take place. No weight can, however, be attached to this, as it is clear from numerous investigations that no such definite stages can be isolated in the cellulose nitrates, and the approximate agreement of the nitrogen percentage is purely accidental (compare, for example, Will, *Ber.*, 1891, **24**, 400). It has been shown by Berl and Fodor (*Zeitsch. ges. Schiess. u. Sprengstoffw.*, 1910, **5**, 254, 269) that the partial decomposition by alkalis is of a much more complex nature.

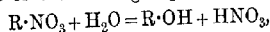
Ample evidence is, however, obtainable in the case of other esters that the nitric group can undergo normal hydrolysis. The following evidence is based partly on acid hydrolysis and partly on alkaline. There appears to be no reason to differentiate, in principle, between these. The same products are obtained in both cases, and as regards the velocity of hydrolysis, it is shown later in the present work that the relationship between acid and alkaline hydrolysis of nitrocellulose is so closely in accord with that of other esters that it can scarcely be supposed that the one is hydrolytic without accepting this for the other.

The data in the present paper refer mainly to the glyceryl nitrates. It is shown, in the first place, that glyceryl trinitrate is hydrolysed by dilute nitric acid under suitable conditions to glycerol, according to the equation



It is also shown that the hydrolysis of glyceryl dinitrate can take place with practically no reduction of the nitric acid and practically no formation of organic acids. It is already known that methyl nitrate is hydrolysed to dimethyl ether by alkali, no internal oxidation taking place. It would be difficult to reconcile this with the primary formation of an aldehyde.

In most cases, hydrolysis is accompanied by much internal oxidation, but this can be overcome in various ways. Thus the normal hydrolysis of the nitric group,



becomes the main reaction whenever the conditions are such that either the oxidising action of the nitric acid is suppressed or the alcohol is rendered immune against oxidation.

Suppression of the Oxidising Action of the Nitric Acid.

(a) *By Reducing Agents.*—In the presence of these, the nitric group cannot oxidise the alcohol, and in this case the alcohol is formed just as in a normal hydrolysis. This is well known in the

case of sulphides (Bloxam, *Chem. News*, 1883, **47**, 169), and was shown by Klason and Carlson (*Ber.*, 1906, **39**, 2752; 1907, **40**, 4183, 4191) to hold also for alkaline hydrolysis in the presence of phenyl mercaptan or hydrogen peroxide. Gutmann (*Ber.*, 1908, **41**, 2052) showed that sodium arsenite acted similarly. Brühl had previously formulated nitric acid and its esters as derivatives of hydrogen peroxide on the basis of spectrometric measurements (*Ber.*, 1898, **31**, 1350), and Klason and Carlson assumed that these esters were hydrolysed to hypothetical alcohol peroxides, which were then reduced to the alcohols. This is a totally unnecessary assumption; their work simply shows that when a reducing agent is present to remove the nascent nitric acid, the normal hydrolysis occurs. The action of hydrogen peroxide seems, indeed, rather incompatible with the assumption of a peroxide, as it is scarcely likely that hydrogen peroxide would react with a derivative of itself in the manner indicated. Cambi (*Atti R. Accad. Lincei*, 1909, [v], **18**, i, 301) has opposed the peroxide formula of nitric acid and its esters. He points out, for instance, that the quantitative oxidation of nitrous to nitric acid by permanganate is not in accordance with this formulation.

(b) *By Sulphuric Acid*.—In the presence of sulphuric acid of moderate strength, the oxidising action of nitric acid is decreased, as is commonly experienced in its action on toluene, etc. If, therefore, nitroglycerin is hydrolysed with 70 per cent. sulphuric acid, the nitric acid does not attack the organic residue to any great extent, and glyceryl dinitrate is formed in good yield (D.R.-P. 175751). Similarly, glyceryl dinitrate is hydrolysed by 70 per cent. sulphuric acid to glyceryl mononitrate and glycerol (Will, *Ber.*, 1908, **41**, 1107).

Protection of the Alcohol from Oxidation.

(a) *By Continuous Abstraction as Glycerophosphoric Acid*.—It is shown in the present work that if glyceryl trinitrate is hydrolysed by phosphoric acid, the glycerol is converted to glycerophosphoric acid, and is thus protected from the oxidising action of the nitric acid. The intermediate formation of an alcohol peroxide or aldehyde appears in this case to be excluded.

(b) *By the Presence of further Nitric Groups*.—When the alcohol contains further nitric groups, it is less susceptible to oxidation than in the absence of such groups. In accordance with this, one of the nitric groups of glyceryl trinitrate can be readily hydrolysed to the alcohol group. Thus, if we represent the group $\text{CH}_2\text{NO}_3\text{CH}$ by R, the decomposition takes the form of a normal hydrolysis, $\text{R}\cdot\text{NO}_3 + \text{H}_2\text{O} = \text{R}\cdot\text{OH} + \text{HNO}_3$. This holds both

for acid and alkaline hydrolysis; thus it is shown in the present work that hydrolysis of glyceryl trinitrate by dilute nitric acid yields glyceryl dinitrate, and Berl and Delpy (*Ber.*, 1910, **43**, 1421) have found the same reaction to take place in the presence of alkalis. Lowry, Browning, and Farmery have conceded that such partial hydrolysis can occur, and it appears strange that with such distinct evidence of the normal hydrolysis of a nitric ester group they should still refuse to recognise this as the first stage in the decomposition.

It is seen, therefore, that whenever the alcohol is protected by any means from oxidation, it is readily obtained as a product of the decomposition. It would be difficult to explain these results in any other way than that the primary reaction is a hydrolysis. This aspect is in no way contrary to the experimental evidence of Lowry, Browning, and Farmery. On the other hand, it is in complete accord with the general nature of the decomposition of nitrocellulose, etc. The whole experience of the behaviour of these esters on storage and in climatic trials (see Silberrad and Farmer, *J. Soc. Chem. Ind.*, 1906, **25**, 961) leaves no doubt that the decomposition is hydrolytic in nature.

Not only is the hydrolysis brought about by the same agencies as in the case of other esters (hydrogen and hydroxyl ions), but the relative velocities are of the order that would be expected for ester hydrolysis. When alkali is added to nitrocellulose, a moderately rapid hydrolysis occurs. The velocity decreases as the alkali is neutralised. When the solution becomes neutral, the hydrolysis becomes very slow, but does not cease entirely, owing to the slight ionisation of the water. Thus the solution gradually becomes acid, and the velocity again increases, but is very much less for the hydrogen ions than for hydroxyl ions, namely, in the ratio of 1 to 480 (Silberrad and Farmer, *T.*, 1906, **69**, 1759). The relative velocities of hydrolysis of esters by acids and alkalis vary somewhat considerably, but the general relationship may be seen from the aliphatic esters examined by de Hemptinne (*Zeitsch. physikal. Chem.*, 1892, **13**, 493). The following table shows the velocity constants at 25°:

	Alkali.	Acid.	Ratio.
Methyl acetate	9.66	0.00659	1466
Ethyl acetate	6.38	0.00682	935
Propyl acetate	5.31	0.00671	791
Ethyl propionate	5.61	0.00727	772
Ethyl butyrate	3.39	0.00417	813

Thus the ratio found for nitrocellulose appears quite reasonable considering that the hydrolysis is abnormal in nature.

In the figure is shown the course of the hydrolysis of nitro-

cellulose in the neighbourhood of the minimum velocity, which is seen to occur slightly on the acid side of the neutral point. The course of the hydrolysis is so characteristic of that of esters that this forms a distinct confirmation of the view that hydrolysis is the primary reaction, both in the presence of acids and of alkalis.

A knowledge of the hydrolytic behaviour of nitric esters has a close bearing on the action of "stabilisers," which are added to explosives (compare Marshall, "Explosives," 1917, p. 640). The idea of adding alkalis to neutralise the acid formed was advocated as early as 1849 (Maurey, *Compt. rend.*, 1849, **28**, 343), and followed up by Abel (*Phil. Trans.*, 1867, 181). It was at first thought that strong alkalis were beneficial to the stability, but it was gradually found that any benefit which these conferred by removing free acid was outweighed by the decomposition to which they themselves gave rise (Kerckhoff, *J. pr. Chem.*, 1847, **40**, 284; Vohl, *Dingl. polyt. J.*, 1849, **112**, 236; Hadow, *T.*, 1854, **7**, 201; Béchamp, *Compt. rend.*, 1855, **41**, 817; *Ann. Chim. Phys.*, 1856, [iii], **46**, 338; Will, *Ber.*, 1891, **24**, 400; Maquenne, *Ann. Chim. Phys.*, 1891, [vi], **24**, 522; Vignon, *Compt. rend.*, 1898, **127**, 872; *Bull. Soc. chim.*, 1903, [iii], **29**, 507; Nef, *Annalen*, 1899, **309**, 181; Lunge, *Zeitsch. angew. Chem.*, 1901, **14**, 578).

Guttmann, on finding that the prolongation of the heat test by alkalis was largely due to "masking" (*J. Soc. Chem. Ind.*, 1897, **16**, 283), went to the other extreme, and contended against Simon-Thomas that all alkalis were harmful (*Zeitsch. angew. Chem.*, 1897, **10**, 233, 265; 1898, **11**, 1003, 1103; 1899, **12**, 55). The behaviour of nitrocellulose, as shown in the figure (p. 817), indicates that neither of these views is correct. The aim of a stabiliser must be to maintain the concentration of hydrogen ions as near as possible to the point of minimum velocity. In practice, this is effected by using such substances as calcium carbonate for the preservation of wet guncotton. Similarly, the salts of numerous organic acids have been used to stabilise pyroxylin (compare Worden, "Nitrocellulose Industry," p. 598).

Non-hydrolytic Decomposition of Nitric Esters.

Although, as indicated above, hydrolysis is the predominating action in presence of water, nitric esters can also undergo other types of decomposition. For the sake of completeness, these should be briefly referred to. They include both catalytic and non-catalytic reactions.

The non-catalytic decomposition of nitrocellulose is best observed by heating in a vacuum or in a current of dry carbon dioxide (Will's test). Under these conditions, volatile catalysts are

removed continuously, and Will has shown (*Zeitsch. angew. Chem.*, 1901, **14**, 743, 774) that if the guncotton is completely purified from substances that would give rise to non-volatile catalysts, such as sulphuric esters, it reaches a limit state, in which the rate of decomposition sinks to a constant minimum for a given degree of nitration. This has been confirmed by Robertson (*J. Soc. Chem. Ind.*, 1902, **21**, 819), and a similar behaviour has been observed by Robertson for nitroglycerin (T., 1909, **95**, 1241). Measurements in a vacuum give similar results.

This non-catalytic decomposition is extremely slow at ordinary temperatures. Extrapolation shows that at 25° the velocity of evolution of nitrogen from guncotton is approximately 0.00125 milligram per gram per year. In other words, the half-life period of guncotton, if we exclude all catalytic influences, is about 70,000 years (that is, the time necessary for the guncotton to lose half its nitrogen, assuming that the rate of loss is maintained).

Apart from the above, a catalytic decomposition can also occur in presence of nitric peroxide. This has been studied mainly in the case of nitrocellulose. It takes place in absence of moisture and accelerates itself autocatalytically. It consists of an internal oxidation of the nitric ester, aided by atmospheric oxygen, which re-oxidises nitric oxide evolved by the nitrocellulose to nitric peroxide. This is absorbed by the nitrocellulose, and causes further decomposition.

Just in the same way as weak alkalis can be added to protect nitric esters from acid hydrolysis, the catalytic decomposition due to nitric peroxide can be combated by the addition of substances which react with nitric peroxide, such as amines, etc. The analogy extends, however, further than this; for in the same way that the acid hydrolysis has its counterpart in a much more rapid alkaline hydrolysis, so also the nitric peroxide catalysis has its counterpart in a much more rapid action of amines (aminolysis). It was thought originally (Hoitsema, *Zeitsch. angew. Chem.*, 1899, **12**, 705) that amines in general might be added with advantage to take up the nitric peroxide, and so act as stabilisers. It is now known that only very weak bases are permissible; aniline, for instance, is much too strong. Diphenylamine is used in many countries with success as a stabiliser of nitrocellulose propellants, and various other weak bases, such as carbamide, diphenyldimethylcarbamide ("centralite"), diphenyldiethylcarbamide (Claessen, D.R.-P. 909546), nitroguanidine (Flemming, *Zeitsch. angew. Chem.*, 1898, **11**, 1053), and many others, have been proposed. The action of amines of the aniline type is very much more rapid than can be accounted for by the direct hydrolysis due

to the hydroxyl ions, thus showing it to be an entirely different type of reaction.

It should be possible to construct a diagram analogous to that given on p. 817 showing the rate of action of nitric peroxide on the one hand (corresponding with acid hydrolysis), and of amines on the other (corresponding with alkaline hydrolysis). Unfortunately, the data necessary for calculating the point of minimum "aminolysis" are not available, but a rough idea of this point can be obtained from the following comparison:

Base.	Affinity constant (25°).	Action on nitrocellulose.
Benzylamine	$2.0 \cdot 10^{-5}$	Inflamed in a few minutes.
Aniline	$5.0 \cdot 10^{-10}$	
Methylaniline	$2.5 \cdot 10^{-10}$	Rapid action. Probably retard decomposition.
Diphenylamine	$5.2 \cdot 10^{-14}$	
Carbamide	$1.5 \cdot 10^{-14}$	

Instead of the affinity constants, it would probably be more correct to take the "aminolytic" constants, as determined, for instance, by Goldschmidt and Salcher's method (*Zeitsch. physikal. Chem.*, 1899, **29**, 89).

EXPERIMENTAL.

Hydrolysis of Nitroglycerin by Nitric Acid.

Six grams of nitroglycerin were warmed on a water-bath with 400 c.c. of 0.2*N*-nitric acid until all the nitroglycerin had disappeared. A small quantity of dissolved nitroglycerin was extracted with ether. After neutralising the aqueous solution with calcium carbonate, filtering, and evaporating, the residue was extracted with acetone. The acetone gave on evaporation a residue containing no nitrogen, and consisting of glycerol, which was identified by conversion to acrolein, by the boric acid test, and by the colour reaction with pyrogallol. It was further converted to glyceryl tribenzoate (m. p. 70°). Oxalic acid was detected by conversion to calcium oxalate and microscopic examination of its crystals, also by the permanganate test. Distillation of the acidified filtrate showed the presence of volatile acids. The distillate reduced silver nitrate and mercuric chloride (formic acid). After elimination of the formic acid by mercuric chloride, the filtrate gave a precipitate on boiling with ferric chloride (probably acetic acid). The solution gave a red colour with Schiff's reagent, but gave no precipitate with phenylhydrazine.

Partial Hydrolysis of Nitroglycerin with Nitric Acid.

In this case, the same quantities were used, but the hydrolysis was interrupted when about two-thirds of the nitroglycerin had

disappeared. The aqueous layer was separated and extracted with ether. The residue obtained on evaporation of the ether was purified by dissolving in a limited quantity of water and removing the residual oil. The aqueous solution was again extracted with ether, and the ether evaporated. The residue contained $N=14.65$, whilst glyceryl dinitrate requires $N=15.39$ per cent.; the product must therefore have retained some mononitrate, which is difficult to separate completely from the dinitrate. It was benzoylated with some difficulty, and the benzoyl derivative melted at 63° and contained $N=10.03$. The quantity was insufficient for further purification, but the substance was evidently the benzoyl derivative of glyceryl $\alpha\alpha'$ -dinitrate, which in the pure state melts at 67° and contains $N=9.79$ per cent. Glyceryl mononitrate was obtained only in small quantity and in an impure state.

Hydrolysis of Nitroglycerin by Phosphoric Acid.

The solution obtained on hydrolysis was neutralised with lime, and filtered from the calcium phosphate which separated. The filtrate yielded on evaporation a syrup, which contained calcium nitrate, and also a soluble calcium salt, from which phosphoric acid and glycerol were obtained. It appears, therefore, to be the calcium salt of glycerophosphoric acid. Further examination of the products of the hydrolysis showed that oxalic acid was absent and formic acid was present only in very small quantity. Practically no oxidation of the glycerol took place.

Hydrolysis of Glyceryl Dinitrate.

In order to ascertain whether the hydrolysis was accompanied by reduction of the nitric acid, a solution of glyceryl dinitrate in nitric acid was maintained at 80° . Separate bottles, each containing 50 c.c. of solution, were used, and these were withdrawn at intervals and a portion titrated. To ascertain whether reduction of the nitric acid occurred, estimations of nitrous acid were also made.

Concentration of Glyceryl Dinitrate = 0.060. Temperature = 80° .

Time (hours).	Concentration of acid (gr. equiv.).	Nitrous acid (mgr.).	Time (hours).	Concentration of acid (gr. equiv.).	Nitrous acid (mgr.).
—	0.200	0.00418	28	0.264	0.0028
4	0.211	—	36	0.275	0.0021
8	0.221	—	44	0.278	0.0084
12	0.232	—	66	0.302	0.0135
16	0.243	—	114	0.312	—
20	0.245	—	—	—	—

The increase in the acidity corresponds with the decomposition of 93 per cent. of the glyceryl dinitrate to glycerol and nitric acid. Very little reduction of nitric acid occurred, as shown by the low proportion of nitrous acid.

In order to ascertain whether the solution contained any acids other than nitric acid, it was extracted with ether to remove unchanged glyceryl dinitrate, and then subjected to reduction. The ammonia was estimated and recalculated to nitric acid. Oxalic and formic acid were also tested for.

	Original (gr. equiv.).	After 114 hours (gr. equiv.).
Nitric acid (NH_3 method) ...	0.1978	0.3005
Formic acid	—	0.0056
Oxalic acid	—	—
Total	—	0.3061
Total acid by titration	0.2000	0.3124

Any other organic acids must thus form less than 2 per cent. of the total acid present.

Formic and Oxalic Acids in Hydrolysis of Cordite.

Several methods were tried for the estimation of formic acid, and the following method was found to be the best. The solution containing formic acid is boiled with a known amount of silver nitrate in the presence of barium carbonate for two hours; excess of standard ammonium thiocyanate solution is then added and the mixture allowed to remain for ten minutes. The solution is filtered, and the excess of thiocyanate estimated in the filtrate by silver nitrate solution. A control test is carried out simultaneously. Tests on known small quantities of formic acid gave satisfactory results.

For the estimations on cordite, 50 grams of the ground cordite were extracted with 100 c.c. of water for two hours on a steam-bath. After filtration and washing, the solution was extracted with ether, neutralised, and evaporated to a small bulk. It was then rendered slightly acid with nitric acid and warmed. Ammonia was added in slight excess and the solution filtered. Calcium nitrate was added and the liquid allowed to remain overnight. Any calcium oxalate was filtered off, dissolved in sulphuric acid, and estimated by permanganate. The filtrate was acidified slightly with sulphuric acid and distilled to recover the formic acid, which was then estimated as above. It was found by separate experiments that no formic acid was destroyed by the nitric acid present.

Cordite.	Formic acid (per cent.).	Oxalic acid (per cent.).
(a)	0.0068	0.0022
(b)	0.0048	0.0019
(c)	0.030	—
(d)	0.037	—
(e)	0.0039	—
(a) After six months at 46° in a wet atmosphere	0.0108	0.0115
(a) After approx. 500 hours at 80°	0.0287	0.239

Minimum Velocity of Hydrolysis of Guncotton.

If the concentration of hydrogen and hydroxyl ions be represented by H and OH , and the velocity-coefficients for acid and alkaline hydrolysis by C_1 and C_2 respectively, the minimum velocity will be reached when $d(C_1H + C_2OH) = 0$ or $d\left(C_1H + C_2\frac{K}{H}\right) = 0$, where K is the water constant $H \times OH$.

$$\text{Now } d\left(C_1H + C_2\frac{K}{H}\right) = C_1dH - \frac{C_2KdH}{H^2} = \\ dH\left(C_1 - \frac{C_2K}{H^2}\right) = dH\left(C_1 - C_2\frac{OH}{H}\right).$$

Experiment shows that the hydrolysis continues to take place through the neutral point, the alkalinity disappearing and acidity being developed; hence dH never becomes equal to zero. From this it follows that $\frac{C_1}{C_2} = \frac{OH}{H}$.

The concentrations at the point of minimum velocity are given by

$$OH = \sqrt{\frac{KC_1}{C_2}}; H = \sqrt{\frac{KC_2}{C_1}}.$$

Data for the velocity-constants are given by Silberrad and Farmer (T., 1906, **89**, 1759). The total velocity of hydrolysis is made up of the sum of the velocities due to hydrogen and hydroxyl ions. The following table shows the velocities in the neighbourhood of the minimum point.

Velocities of Hydrolysis of Guncotton at Low Concentrations of Hydrogen Ions. (Equivalent per litre per hour. At 37.8°.)

H-ions conc. (10 ⁻³)	OH-ions conc. (10 ⁻³)	Velocity.		
		Due to H-ions. (10 ⁻³)	Due to OH-ions. (10 ⁻³)	Total. (10 ⁻³)
0.5	58.0	0.44	24.00	24.44
1.0	29.0	0.87	12.00	12.87
2.0	14.5	1.74	6.00	7.74
3.0	9.7	2.61	4.00	6.61
3.7	7.8	3.25	3.25	6.50
5.0	5.8	4.35	2.40	6.75
10.0	2.9	8.70	1.20	9.90
20.0	1.45	17.40	0.60	18.00

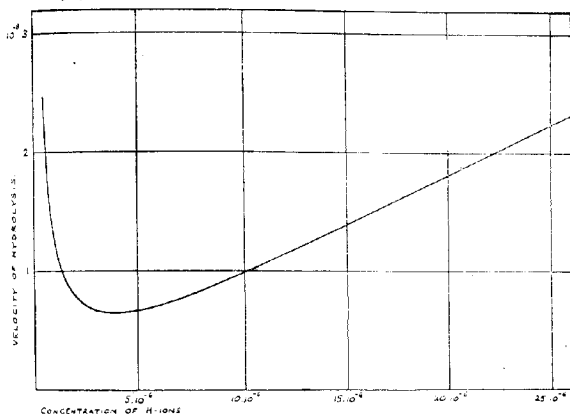
The course of the hydrolysis is shown in the figure. The minimum velocity is seen to lie distinctly on the acid side of the

neutral point. The acidity is comparable with that of a 0.1*N*-solution of phenol.

Decomposition of Nitrocellulose in the Presence of Amines.

To illustrate the decomposing action of organic bases as compared with alkaline salts, the following examples may be given. Fifty grams of nitrocellulose were enclosed in a vessel of 100 c.c. capacity, and the alteration of gas volume was measured by a gas

Velocity of hydrolysis of nitrocellulose at 37.8° (equivalent per litre per hour).



burette at the ordinary temperature (mean=16°). The contraction is due to the formation of nitric oxide, which absorbs oxygen from the air. In each case, 5 per cent. of admixture was taken.

Alteration in Gas Volume at 16° (c.c. corr.).

Days.	2.7.	4.6.	7.0.	12.	18.	20.	33.
Sodium carbonate	—	+0.15	+0.10	-0.05	-0.10	-0.25	-0.35
Methylaniline ...	-4.6	-5.65	-6.80	-8.30	-9.90	-10.45	-11.85

The nitrocellulose itself showed only a very slight contraction. When it was mixed with diphenylamine, the contraction was also very slight. On attempting to make measurements with benzylamine, the decomposition was so rapid that the nitrocellulose inflamed in a few minutes.

Affinity Constant of Diphenylamine.—This did not lend itself to the ordinary methods of determination, but can be deduced from the solubility of diphenylamine in water and in acid.

	Gram per litre.	Gram-molecule per litre.
Solubility in water at 25°	0.0462	0.0002734
" " 0.211 <i>N</i> -HCl at 25°	0.0174	0.0002805
	0.0855	0.000507
		H H

The concentration of hydrogen ions in 0.211*N*-hydrochloric acid is 0.192. Assuming the diphenylamine hydrochloride at the above high dilution to be completely ionised, the hydrolytic constant

$$\frac{\text{acid} \times \text{base}}{\text{salt}} = \frac{0.1917 \times 0.000277}{0.000230} = 0.230$$

and the affinity constant of the free base is equal to 5.2×10^{-14} , taking the ionisation of water as 1.09×10^{-7} .

Summary.

The different forms of decomposition of nitric esters can be classified as follows:

- (1) Decomposition of the pure ester.
- (2) Accelerated decomposition.
 - (a) Hydrolysis (followed by internal oxidation):
 - (i) by acids (slow but autocatalytically accelerated);
 - (ii) by alkalis (relatively rapid).
 - (b) Internal oxidation in absence of water:
 - (i) by nitric peroxide (slow but autocatalytically accelerated);
 - (ii) by amines, etc. (relatively rapid).

The hydrolytic decomposition passes through the following phases:

- (i) Incipient ester hydrolysis.
- (ii) Internal oxidation, possibly to an alcohol peroxide (although this is speculative).
- (iii) Formation of an aldehyde.
- (iv) Decomposition to hydroxy-acids.

When the conditions are such that the alcohol is protected from oxidation, it is readily regenerated as such on hydrolysis, thus showing that the first stage in the decomposition is a true ester hydrolysis of the normal type. The hydrolysis is shown to resemble that of other esters in its general relationship between velocity and concentration of hydrogen or hydroxyl ions, and the bearing of this relationship on the stabilisation of nitric esters is shown.

The author's thanks are due to Mr. H. J. Merriman for permission to include experiments on nitroglycerin and cordite, and to the Director of Artillery for his sanction for the publication of the work.

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Organic Chemistry.

The Chemical Mechanism of Organic Rearrangements.

ARTHUR MICHAEL (*J. Amer. Chem. Soc.*, 1920, **42**, 787-821).—

A theoretical paper dealing with rearrangement as determined by the affinity, energy, and spatial relationships of the atoms involved. Intramolecular rearrangements are determined by the free chemical energy at the interchanging atoms or groups, their affinity for each other and for the atoms in the groups to which they migrate, the amount of energy required to separate the migrating portion from the remaining atoms of the group, and the heats of formation of the isomerides or the two products. In a heterogeneous chemical system, change in chemical structure of a compound may be due to catalytic influence or to chemical action of the energy in the reagent employed, involving loss of a component part of the compound and subsequent isomerisation of the residual structure. A polymolecule may be produced by union of the compound with the reagent, when, owing to the chemical energy so added, isomerisation in the compound portion of the product takes place, resulting in partial conversion of its free energy into bound energy and heat, and subsequent decomposition of the system into the isomerised product and the reagent. These considerations are applied to critical reviews, which do not lend themselves to abstraction, of the various hypotheses proposed in explanation of the Hofmann conversion of bromoamides into primary amines, the rearrangements of aliphatic and aromatic $\alpha\beta$ -glycols under the influence of acid, the pinacolin change, the rearrangements of aryl iodohydrins, and the formation of benzoic acid from benzil. A general consideration is also given of the production of intermediate products in such reactions. In regard to the question as to whether elimination of groups of atoms, for example, hydrogen and bromine from ethyl bromide, takes place from the same carbon atom or from more than one, it is concluded that, generally speaking, the former is of rare occurrence, because the latter usually results in a greater increase in entropy.

J. K.

Oxidative Decomposition of Hydrocarbons. H. HEINRICH

FRANCK (*Chem. Zeit.*, 1920, **44**, 309-310).—Aliphatic hydrocarbons of high molecular weight, such as paraffin oils and waxes, are oxidised to carboxylic acids and other oxidation products when decomposed by heat in the presence of oxygen and a catalyst. By varying the conditions of the oxidation, different proportions of volatile and non-volatile fatty acids may be obtained. Good results are obtained by the use of compounds of lead, mercury, manganese, vanadium, and chromium as catalysts, whilst alkalis and alkaline earths may also be used. In practice, good yields of fatty acids, ranging from acetic to arachidic acid, may be obtained by heating

paraffin wax in an autoclave at 150° in the presence of oxygen and 0.5 to 5% of catalyst, although eventually the oxidation may also be effected without a catalyst. The resulting fatty acids were separated by converting them into esters, which were fractionally distilled. The product obtained from an expressed paraffin-wax residue yielded 57.1% of fatty acids of lower molecular weight and 40.7% of acids of higher molecular weight, and contained unsaponifiable matter, from which a ketone melting at $46-50^{\circ}$, probably a mixture of stearone with other ketones, was separated. An edible fat resembling coconut oil was prepared by esterifying the mixed fatty acids thus obtained with ethylene glycol and 3% of sulphuric acid. [See, further, *J. Soc. Chem. Ind.*, 1920, 395a.]
C. A. M.

Brodie's Myricyl Alcohol. ALBERT GASCARD (*Compt. rend.*, 1920, 170, 886-888).—Brodie attributed to the myricyl alcohol obtained from beeswax the formula $C_{30}H_{61}\cdot OH$. The author has prepared this alcohol and the corresponding iodide, and from careful analyses of the latter, and by preparation of the corresponding saturated hydrocarbon and comparison of the properties of the alcohol and its derivatives with known compounds in a near position in the same series, he concludes that myricyl alcohol has the formula $C_{31}H_{63}\cdot OH$. Finally, from lacceric [dotriacontanoic] acid, $C_{32}H_{65}\cdot CO_2H$ (A., 1914, i, 1045), he has prepared myricyl alcohol by degradation, and from myricyl alcohol, by conversion into the cyanide and hydrolysis, obtained lacceroic acid.
W. G.

The Equation of State of Ethyl Ether. E. ARIÈS. (*Compt. rend.*, 1920, 170, 871-875).—By the use of equations already established, the author has calculated the saturated vapour pressures and the differences of the molecular volumes of the saturated fluid for ethyl ether for each 10° from -10° to 190° , and his results are in fairly close agreement with those obtained by Young. Finally, he finds for the heat of vaporisation of ethyl ether at 30° the value 85.63 cal., the value given by Young being 85.18 cal.
W. G.

The Decomposition of Nitric Esters by Lime. THOMAS MARTIN LOWRY, KENDALL COLIN BROWNING, and JOSHUA WILLIAM FARMERY (T., 1920, 117, 552-561).

Action of the Normal Methyl and Ethyl Sulphates on the Alkali Phosphates in Aqueous Solution. OCTAVE BAILLY (*Compt. rend.*, 1920, 170, 1061-1064).—Methyl sulphate reacts with an aqueous solution of trisodium phosphate to give 77.8% of disodium methyl phosphate and 6.2% of sodium dimethyl phosphate, the former being converted into its barium salt, which may readily be isolated. With ethyl sulphate, the yield of the monoethyl phosphate is much lower and of the diethyl phosphate slightly higher. If disodium hydrogen phosphate is used in place of the trisodium salt, the total yield of the esters is lower, and sodium

dihydrogen phosphate or phosphoric acid does not react in aqueous solution with methyl or ethyl sulphate.

W. G.

The Constitution of the Glycerophosphoric Acids. OCTAVE BAILLY (*Bull. Soc. chim. biol.*, 1919, 1, 152—162).—By decomposition of barium glycerophosphate, obtained from lecithin, with sodium carbonate in aqueous solution, a solution of sodium glycerophosphate was obtained, which was separated into two fractions, one crystalline and the other non-crystalline.

The non-crystalline fraction gave a calcium salt, which yielded on oxidation with bromine water evidence of the formation of an ether of dihydroxyacetone. This points to the calcium salt being a salt of α -glycerophosphoric acid. The crystalline sodium salt appears to be a derivative of the β -acid. Therefore the glycerophosphoric acid obtained by the hydrolysis of lecithin is a mixture of the two isomerides.

J. C. D.

Action of Water on $\beta\beta'$ -Dichlorodiethyl Sulphide. CH. BOULLIN and L. J. SIMON (*Compt. rend.*, 1920, 170, 845—848).— $\beta\beta'$ -Dichlorodiethyl sulphide is slowly decomposed by cold water and rapidly by boiling water, giving hydrochloric acid and dihydroxydiethyl sulphide. The reaction is an equilibrium phenomenon, and is considerably influenced by the temperature and the relative proportions of dichlorodiethyl sulphide and water used. Both acids and alkalis exert a retarding influence on the decomposition.

The solubility of dichlorodiethyl sulphide in cold water is 0.48 gram per litre. It is increased by the presence of dihydroxydiethyl sulphide. The presence of the latter in small amounts also accelerates the decomposition of dichlorodiethyl sulphide, but as its concentration increases, the velocity of decomposition decreases.

W. G.

Sulphur Derivatives of Butyl Alcohol. H. LEB. GRAY and GURNEY O. GUTEKUNST (*J. Amer. Chem. Soc.*, 1920, 42, 856—860).—Dibutyl sulphide is best prepared by boiling aqueous solutions of sodium butyl sulphate and sodium sulphide in a reflux apparatus, and subsequently distilling; if the mixture is distilled without previous boiling, butyl mercaptan is also produced. The method of oxidation of the sulphide to the sulphone by nitric acid, recommended by Grabowsky (1874), is untrustworthy, but excellent results are obtained by the use of sodium permanganate in neutral solution.

J. K.

Catalytic Decomposition of Fatty Acids by Carbon. J. B. SENDERENS and J. ABOULENC (*Compt. rend.*, 1920, 170, 1064—1067).—When acetic acid or its homologues are passed over purified animal charcoal at 360—380°, the acids are decomposed, giving a mixture of carbon dioxide, ethylenic hydrocarbons, carbon monoxide, methane and its homologues, and hydrogen, together with water and small amounts of ketones and aldehydes. With carbon from sugar, a considerably higher temperature is necessary, but the products are much the same.

W. G.

Remarkable Similarity in the Form of Crystals and Microbes. ARMINIUS BAU (*Zeitsch. techn. Biol.*, 1919, 7, 203—213; from *Chem. Zentr.*, 1920, i, 495).—With the aid of microphotographs (magnification, 1000 times), the author describes crystals of calcium oxalate which differ from the usual crystals in such a manner that they can easily be mistaken for *Saccharomycetes* or rod-like bacteria. The crystals are obtained by precipitation of solutions containing oxalic acid with calcium acetate, and may readily be distinguished from living matter by their ready solubility in moderately dilute hydrochloric, nitric, or sulphuric acid.

H. W.

Preparation of Fat and Wax-like Substances. FARBEN-FABRIKEN VORM. FRIEDR. BAYER & Co. (D.R.-P. 318222; from *Chem. Zentr.*, 1920, ii, 536).—Adipic acid or its derivatives or homologues is esterified with dihydroxylated hydrocarbons or their derivatives. *Glycyl adipate* is obtained as a tallow-like mass when adipyl chloride dissolved in pinacolin is treated with a solution of ethylene glycol and pyridine in the same solvent; the ester may also be prepared from ethylene dibromide and potassium adipate. *Glycyl α-methyladipate*, brown, waxy mass, is obtained from ethylene oxide and α-methyladipic acid. *Propyleneglycyl adipate*, from propylene iodide and potassium adipate, resembles butter.

H. W.

The Supposed Methanetetra-carboxylic Acid. EYVIND BÆDTKER (*Bull. Soc. chim.*, 1920, [iv], 27, 257—258).—The substance previously described as methanetetra-carboxylic acid (compare A., 1916, i, 2) is now shown to be ammonium tetraoxalate.

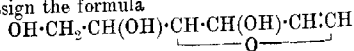
W. G.

Preparation of Glyoxal. ALEXANDER BOSSHARD (Brit. Pat. 140478).—When ozone acts on acetylene in presence of a large proportion of air, oxygen, or other indifferent gas, the reaction ceases to be violent in character and results in the production of glyoxal. Proportions which have been found successful are 1—2% of ozone, 3—4% of acetylene, and 94—96% of air. The process is facilitated by the presence of water vapour or the use of a water spray, whereby the glyoxal is washed out of the gaseous mixture and separates as a concentrated solution.

G. F. M.

Experiments on the Preparation of Oximino-derivatives. WILLIAM KERSHAW SLATER (T., 1920, 117, 587—591).

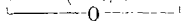
Glucal and its Conversion into New Substances of the Dextrose Series. EMIL FISCHER, MAX BERGMANN, and HERBERT SCHOTTE (*Ber.*, 1920, 53, [B], 509—547).—A further study of glucal and its derivatives (A., 1913, i, 445; 1914, i, 252) leads the authors to assign the formula



to the parent substance, for the following reasons. Glucal triacetate can be converted into *d*-glucosephenylosazone, thus showing that glucal contains the normal carbon chain present in dextrose, and also that a saturated carbon atom unattached to oxygen is not present. The transformation of glucal triacetate into *d*-arabinose by means of ozone proves the double bond to be between the first and second atoms of the carbon chain. The presence of the furan ring accounts for the colour reaction with a pine shaving and the observed individuality of one of the acetyl groups of glucal triacetate. Only three oxygen atoms of hydroglucal are present in hydroxyl groups, and the stability of the substance towards hydrochloric acid renders the presence of an ethylene or trimethylene oxide ring improbable. The location of the tetramethylene ring in the glucal molecule is deduced from the smooth conversion of glucal triacetate into a derivative of dextrose, and from the proof that the carbon atom, 6, does not participate in the formation of glucal.

Glucal triacetate is transformed by ozone in glacial acetic acid solution into *d*-arabinose triacetate and the triacetyl derivative of pentanetetrollic acid (probably arabonic acid), long needles or prisms, m. p. 127° after much softening at 120°, $[\alpha]_D^{25} + 27.23^\circ$ in alcoholic solution; the former showed little tendency to crystallise, and was therefore immediately hydrolysed to *d*-arabinose, which was identified as the *p*-bromophenylhydrazone and the phenylbenzylhydrazone, colourless, shining leaflets, m. p. 177–178° (corr.), $[\alpha]_D^{25} + 14.4^\circ$ in methyl alcohol.

Glucal triacetate is converted into *d*-glucosephenylhydrazone by the following process. The additive product of bromine and glucal triacetate (Fischer, *loc. cit.*) is treated with silver acetate, and thus converted into a mixture of stereoisomeric tetra-acetylglucose-*B*-chromohydrins, $\text{OAc}\cdot\text{CH}_2\cdot\text{CH}(\text{OAc})\cdot\text{CH}\cdot\text{CH}(\text{OAc})\cdot\text{CHBr}\cdot\text{CH}\cdot\text{OAc}$,

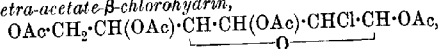


which is deacetylated by dilute hydrochloric acid and then treated with phenylhydrazine; the yield is about 60%.

Glucal triacetate reacts with a saturated solution of hydrogen bromide in glacial acetic acid to yield *glucal diacetate hydrobromide*, slender needles, m. p. 99–100°; the substance exhibits mutarotation in acetylene tetrachloride, chloroform, or alcohol, but is recovered unchanged from its solutions. It contains a free hydroxyl group, since it is transformed by acetic anhydride in the presence of pyridine into *glucal triacetate hydrobromide*, prisms, m. p. 82–85°, $[\alpha]_D^{25} + 54.43^\circ$ in tetrachloroethane, which does not show mutarotation. The constitution of these substances has not been definitely elucidated.

The addition of bromine to glucal triacetate yields a mixture of unstable dibromides, from which on some occasions it has been found possible to isolate a crystalline compound, $\text{C}_{12}\text{H}_{16}\text{O}_7\text{Br}_2$, m. p. 17–118° (corr.), which, however, was not optically homogeneous and the isolation of which could not be subsequently effected after loss of seeding material. The corresponding *dichloride* proved to be more stable, but in spite of homogeneous appearance and

constant, if slightly indefinite, m. p. (92—94°), it was likewise not optically uniform, and appeared to consist of a mixture of varying proportions of stereoisomerides; the most active preparation had $[\alpha]_D^{25} + 199.7^\circ$ in tetrachloroethane solution. The dichloride is transformed by silver acetate in glacial acetic acid solution into *glucosetetra-acetate-β-chlorohydrin*,



monoclinic-sphenoidal crystals, $a : b : c = 0.7786 : 1.07030$, $\beta = 117^\circ 53\frac{1}{2}'$, m. p. 110—111°, $[\alpha]_D^{18} + 51.1^\circ$ in tetrachloroethane.

Crude glacial triacetate dibromide is converted by methyl alcohol and silver carbonate into a mixture of *triacetylmethylglucoside-β-bromohydrins*: (1) rhombic, bisphenoidal crystals,

$$a : b : c = 0.2602 : 1.0 : 2855,$$

m. p. 139° (corr.), $[\alpha]_D^{18} + 50.2^\circ$ in tetrachloroethane, and (2) monoclinic, sphenoidal crystals, $a : b : c = 2.7028 : 1 : 1.6237$, $\beta = 99^\circ 52'$, m. p. 115—116°, $[\alpha]_D^{18} - 92.0^\circ$ in tetrachloroethane. The acetyl compounds can be deacetylated by methyl-alcoholic ammonia, and yield the corresponding *methylglucoside-β-bromohydrins*: (1) m. p. 181—182° (slight decomp.), $[\alpha]_D^{18} + 0.87^\circ$ in aqueous solution, and (2) m. p. 182—183° (corr.; decomp.), $[\alpha]_D^{18} - 63.8^\circ$ in aqueous solution; the former does not reduce Fehling's solution and is stable towards *N*-hydrochloric acid, whereas the latter is readily attacked. *Triacetylmethylglucoside-β-chlorohydrin*, thin prisms, m. p. 150—151° (corr.), $[\alpha]_D^{18} + 40.0^\circ$ in tetrachloroethane, is very readily obtained from glacial triacetate dichloride, only one modification appearing to be formed. On deacetylation, it gives *methylglucoside-β-chlorohydrin*, slender needles, m. p. 164° after softening at about 159°, $[\alpha]_D^{18} - 12.05^\circ$ in aqueous solution.

Methyl epiglucosamine, $\text{OMe} \cdot \text{C}_6\text{H}_{10}\text{O}_4 \cdot \text{NH}_2$, is obtained in the form of its salts by the action of hot aqueous ammonia on methylglucoside-β-bromohydrin (1) or methylglucoside-β-chlorohydrin; the *hydrobromide* crystallises in needles, m. p. about 215° (decomp.). $[\alpha]_D^{25} - 123.8^\circ$ in aqueous solution, whilst the *hydrochloride* decomposes at 210—211° and has $[\alpha]_D^{25} - 146.6^\circ$ in water. The glucoside is not attacked by emulsin or yeast extract. Methyl epiglucosamine could only be isolated as a syrup. *Tetra-acetylmethyl epiglucosamine* is, however, smoothly obtained when the above hydrochloride is treated with acetic anhydride and dry pyridine at the ordinary temperature; it forms rhombic-bisphenoidal crystals, $a : b : c = 0.4279 : 1.0 : 3906$, m. p. 188°, $[\alpha]_D^{18} - 119.2^\circ$ in chloroform, and does not appear to be identical with the tetra-acetylmethylglucosamine described by Hamlin.

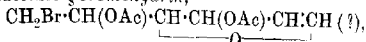
Treatment of either form of methylglucoside-β-bromohydrin with sodium amalgam and water (the chlorohydrin, however, is only extremely slowly affected) leads to the formation of *β-deoxymethylglucoside*, $\text{OMe} \cdot \text{CH} \cdot \text{CH}_2 \cdot \text{CH}(\text{OH}) \cdot \text{CH} \cdot \text{CH}(\text{OH}) \cdot \text{CH}_2 \cdot \text{OH}$, which, in

$\begin{array}{c} \text{O} \\ \text{---} \end{array}$

the absence of seeding material, is best purified through the triacetyl derivative; the pure substance has m. p. 122—123° (corr.).

$[\alpha]_D^{17} - 48.22^\circ$ in aqueous solution. It does not reduce Fehling's solution, but is readily hydrolysed by *N*/10-hydrochloric acid, but not by yeast extract or emulsin. *Triacetyl-β-deoxymethylglucoside* forms rhombic-bisphenoidal crystals, $a : b : c = 0.4701 : 1.0 : 0.5636$, *m. p.* $96-97^\circ$ after softening at 91° . $[\alpha]_D^{19} - 30.31^\circ$ in tetrachloroethane solution.

Glucal diacetate-ξ-bromohydrin,



needles, *m. p.* $44-45^\circ$, $[\alpha]_D^{18} - 43.03^\circ$ in tetrachloroethane, is obtained by the reduction of acetyldibromoglucose with zinc dust and acetic acid. It reduces Fehling's solution, adds bromine in chloroform solution, and gives a green coloration with a pine shaving; it does not, however, restore the colour of a magenta-sulphurous acid solution. H. W.

A Celloisobiose. H. OST and R. PROSIEGEL (*Zeitsch. angew. Chem.*, 1920, **33**, 100).—A new biose has been isolated from the product of the acetylation of cellulose in presence of considerable quantities of sulphuric acid, the reaction being allowed to proceed for some days at 30° , or for some weeks at $15-20^\circ$, until crystals of the known cellobiose octoacetate begin to separate. *Celloisobiose*, $\text{C}_{12}\text{H}_{22}\text{O}_{11}$, is easily soluble in water, sparingly so in alcohol, and forms fine needles, which melt indefinitely at $165-190^\circ$ with evolution of gas; in aqueous solution, $[\alpha]_D + 23^\circ$. It has a slightly sweet taste, and its reducing property is 99% of that of maltose. It is not hydrolysed by yeast, but readily yields dextrose when treated with hydrochloric acid. Whilst cellobiose showed signs of fermentation after five days (compare, however, Schliemann, *Diss.*, Hanover, 1910), *celloisobiose* gave no carbon dioxide. J. K.

The Viscosity of Solutions of Cellulose. I. WILLIAM HOWIESON GIBSON. II. WILLIAM HOWIESON GIBSON [with LEO SPENCER and ROBERT MCCALL] (*T.*, 1920, **117**, 479-493).

Digestive Hydrolyses by Mechanical Ionisation of the Water. J. E. ABELOUS and J. ALOY (*Compt. rend.*, 1920, **170**, 1012-1014. Compare A., 1919, i, 310).—Simple shaking or bubbling of air through an aqueous solution or suspension of starch, lactose, neutral fats, or fibrin produces a partial hydrolysis, the amount increasing with rise in temperature. The addition of boiled digestive juices, such as saliva in the case of starch, or gastric juice in the case of fibrin, considerably increases the hydrolysis, although the enzymes in these juices were destroyed by the preliminary boiling. W. G.

The Supposed Fission of Starch by Formaldehyde. M. JACOBY, W. VON KAUFMANN, A. LEWITE, and H. SALLINGER (*Ber.*, 1920, **53**, [B], 681-685).—A reply to Woker's recent criticisms (this vol., i, 10). The simple explanation of the supposed diastatic action of formaldehyde lies in the fact that the latter forms a loose additive compound with starch (which does not give a blue color-

ation with iodine), and also modifies the physical properties of the colloid; precipitation with alcohol, or with numerous electrolytes which behave similarly, yields unchanged starch, which under no conditions has suffered diastatic degradation. H. W.

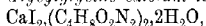
Some Properties of Inulin and Changes in its Physical State. J. WOLFF and B. GESLIN (*Bull. Soc. chim. biol.*, 1920, 2, 19—23).—The hydrolysis of inulin is considered. Inulin prepared from chicory or dahlias is more soluble in water than that from other sources after it has been precipitated by alcohol. It can be converted into the less soluble form by evaporating the solution. The change is reversible, and is not fully understood.

J. C. D.

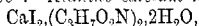
The Diastatic Hydrolysis of Inulin. H. COLIN (*Compt. rend.*, 1920, 170, 1010—1012).—In the hydrolysis of inulin by inulase from different sources, there is no indication of the formation of any intermediate products between inulin and the reducing sugars.

W. G.

Preparation of Organic Derivatives of Calcium Iodide. WALTER SPITZ (D.R.-P. 318343; from *Chem. Zentr.*, 1920, ii, 601).—Aqueous or alcoholic solutions of calcium iodide are allowed to react with neutral aqueous or alcoholic solutions of organic derivatives of ammonia, such as free or combined amino-acids or carbamides, and the additive compounds are obtained in the solid state by evaporation or spontaneous crystallisation of the solutions. *Glycine calcium iodide*, $\text{CaI}_2 \cdot \text{NH}_2 \cdot \text{CH}_2 \cdot \text{CO}_2\text{H} \cdot 2\text{H}_2\text{O}$, crystallises from aqueous solutions of the components in colourless, prismatic needles which decompose, without melting, above 275° ; the iodine is not completely precipitated by silver nitrate in nitric acid solution. *Carbamide calcium iodide*, $\text{CaI}_2 \cdot \text{CO}(\text{NH}_2)_2 \cdot 2\text{H}_2\text{O}$, obtained by boiling an aqueous solution of the components with a few drops of acetic acid under reflux, forms large, transparent plates, m. p. 167.5° ; the calcium is quantitatively precipitated by ammoniacal ammonium oxalate. *Glycylglycine calcium iodide*,



colourless needles, decomposes with separation of iodine, but without melting, above 200° . *Alanine calcium iodide*,



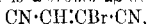
has m. p. 115° . The compounds are stable in air, not hygroscopic, and applicable in pharmacy; in contrast to calcium iodide, they are not decomposed by carbon dioxide.

H. W.

Action of Chlorine, of Hypochlorous Acid, and of Cyanogen Chloride on Cyanamide and its Derivatives. CH. MAUGUIN and L. J. SIMON (*Compt. rend.*, 1920, 170, 998—1001).—When chlorine is passed over cyanamide, a yellow, highly polymerised product is obtained. When the gas is passed into an aqueous solution of the amide or of calcium cyanamide, a lachrymatory product is obtained. If the solution is then warmed, a red vapour is given off, which condenses below 0° to a red, extremely unstable liquid.

which explodes after a few minutes. When an aqueous solution of cyanamide is added gradually to an aqueous solution of hypochlorous acid free from chlorine, and the mixture cooled to 0° , a very unstable, crystalline product, dangerous to handle, is obtained. When perfectly dry silver cyanamide is added to an excess of cyanogen chloride at 0° , a white powder is formed, which is a silver compound, $\text{AgN}(\text{CN})_2$, and swells up when heated. This silver compound is decomposed by hydrogen chloride in ethereal solution, giving *dicyanimide hydrochloride*, $\text{NH}(\text{CN})_2\cdot\text{HCl}$, which in its turn is decomposed by water to give biuret. If the silver compound, $\text{AgN}(\text{CN})_2$, is decomposed in water by dilute hydrochloric acid, it gives *cyanocarbamide*, $\text{CN}\cdot\text{NH}\cdot\text{CO}\cdot\text{NH}_2$. W. G.

Carbon Subnitride. Action of Halogens, of the Hydrohalogen Acids, and of Alcohols. CHARLES MOUREU and JACQUES CH. BONGRAND (*Compt. rend.*, 1920, **170**, 1025—1028. Compare A., 1914, i, 671).—The heat of combustion of carbon subnitride agrees with the equation $4\text{C}_{\text{diamond}} + \text{N}_{2\text{gas}} = \text{C}_4\text{N}_{2\text{solid}} - 138.3 \text{ cal.}$ The subnitride fixes all the halogens. With an aqueous solution of hydrobromic acid, the product is *α -bromo- $\alpha\beta$ -dicyanoethylene*,



m. p. $48.5\text{--}49^{\circ}$. Similarly, the subnitride adds on the elements of hydrogen iodide, giving *α -iodo- $\alpha\beta$ -dicyanoethylene*, m. p. $86\text{--}87^{\circ}$. With hydrochloric acid, partial hydrolysis also occurs, and the product is *chloro- β -cyanoacrylamide*, m. p. 167° , the chlorine probably being attached to the α -carbon atom. When carbon subnitride is treated with absolute alcohol, it yields *α -ethoxy- $\alpha\beta$ -dicyanoethylene*, m. p. $30.5\text{--}31^{\circ}$, $D_{4}^{25} 1.0166$, $n_D^{25} 1.4677$. Similar additive products are obtained with other alcohols. W. G.

Preparation of Cyanogen Chloride on a Large Laboratory Scale. T. SLATER PRICE and STANLEY J. GREEN (*J. Soc. Chem. Ind.*, 1920, **39**, 98T—101T).—The most convenient method for the preparation of cyanogen chloride on a large laboratory scale is by the action of chlorine on a dilute solution (12—15%) of hydrocyanic acid. The chlorine is forced into the solution through a porous pot, and the fine bubbles so produced bring about rapid chlorination. The heat of reaction is sufficient to distil over the cyanogen chloride into cooled receivers; the crude product contains water and hydrogen cyanide, together with traces of hydrochloric acid; methods of purification are described.

Instead of using a pure solution of hydrocyanic acid, the acid may be made in situ by the interaction of sodium cyanide and sulphuric acid solutions, the hydrocyanic acid solution thus produced being about 6% strength. On a large scale, this method suffers from the disadvantage that considerable cooling is necessary during the preparation of the solution of hydrocyanic acid.

The method described by Jennings and Scott (A., 1919, i, 526) is not practicable on a large scale, owing to the difficulty of regulating the temperature.

It is shown that the reaction between chlorine and hydrocyanic

acid proceeds quantitatively according to the equation $\text{Cl}_2 + \text{HCN} \rightleftharpoons \text{CNCl} + \text{HCl}$.

Pure cyanogen chloride has b. p. 13° (uncorr.) and m. p. -80° , D₄ 1.207, and D₃ 1.218. By the action of hydrogen chloride, the following effects are produced: (a) The cyanogen chloride is polymerised to cyanuric chloride, the reaction taking place slowly and only to any extent in the absence of water. (b) Hydroxylation of the cyanogen chloride to cyanic acid and carbon dioxide, and hence to ammonium chloride and carbon dioxide. This is a much more rapid reaction than (a), the velocity increasing with the strength of the acid. The action is complete in a few hours with 9*N*-HCl; with 2*N*-acid, the reaction is very slow, and even with 5*N*-acid takes several days. The pure substance does not undergo polymerisation, and dry chlorine and carbonyl chloride have no action on it.

In an addendum, a small-scale continuously acting apparatus is described.

T. S. P.

Methylstannonic Acid and some of its Salts and Derivatives. J. G. F. DRUCE (*Chem. News*, 1920, 120, 229—230).—

In view of the suggestion that potassium hydrogen stannite has a structure similar to that of potassium formate (Hantzsch, A., 1902, ii, 289), the relationship of methylstannonic acid to acetic acid has been studied, but they are found to have little in common. The corresponding methylstannonates are precipitated on the addition of copper, zinc, nickel, or ferrous sulphates to solutions of the alkali salts. The acid is insoluble in solutions of the alkaline carbonates or in organic solvents, but soluble in mineral acids, acetic and tartaric acids. It is infusible, but when strongly heated is decomposed into stannic oxide, methane being also produced in absence of air. Stannic oxide is also produced when the acid is gently heated with ammonium nitrate. A modification of Pfeiffer and Lehnardt's method of preparing the acid (A., 1903, i, 470, 802) consists in the careful acidification of the residual solution after removal of alcohol at 40° from the product of the action of methyl iodide on an alcoholic potassium stannite solution at the ordinary temperature for three days. Methylstannoyl potassium carbonate, which is produced by Pfeiffer's process, forms crystalline platelets, the solution of which in water is alkaline in reaction and suffers decomposition either by heat or by dilute hydrochloric acid, carbon dioxide being produced in the latter case. *Aniline methylstannichloride*, $(\text{NH}_2\text{Ph})_2\text{H}_2\text{MeSnCl}_5$, prisms, m. p. 214° , from tin methyl chloride or methylstannonic acid and aniline hydrochloride, forms an acid solution, unaltered by boiling. *Methylaniline methylstannichloride*, $(\text{NHMePh})_2\text{H}_2\text{MeSnCl}_5$, granules, m. p. 194° . *Pyridine methylstannichloride*, $\text{Py}_2\text{H}_2\text{MeSnCl}_5$, yellow plates, m. p. 300° . J. K.

Catalytic Oxidation. I. Benzene. JOHN MORRIS WEISS and CHARLES R. DOWNS (*J. Ind. Eng. Chem.*, 1920, 12, 228—232. Compare this vol., i, 216, 236).—An outline of investigations of

the catalytic oxidation of benzene, especially the formation of maleic acid. In this reaction, using vanadium dioxide as catalyst, temperature control is the most important factor. The apparatus employed consisted essentially of a vaporiser and mixer, a contact tube, and a condensing system; the contact tube was immersed in a metal bath kept at a definite temperature. W. P. S.

The Introduction of the Chloromethyl Group into the Aromatic Nucleus. HENRY STEPHEN, WALLACE FRANK SHORT, and GEOFFREY GLADDING (T., 1920, 117, 510—527).

[Freezing Points of Binary and Ternary Systems of Nitrotoluenes.] E. CHABANIER (*Mon. Sci.*, 1920, [v], 10, 80).—The method of determining the freezing points of component systems of nitrotoluenes described by Bell and Herty (this vol., i. 152) is the most trustworthy yet devised; but to obtain concordant results, the supercooling must not be too pronounced, since the temperature does not subsequently rise to the same extent as when there is only slight supercooling. Owing to the variable influence of supercooling, the melting-point curves thus obtained will be slightly below the true curves for binary systems. Applying the hypothesis of Bell and Herty, the eutectic points of binary mixtures of 2:3-, 2:4-, 2:5-, and 2:6-dinitrotoluenes have been calculated. The method is also applicable to the study of nitration processes. For example, direct nitration of toluene to dinitrotoluene gives mixtures of 2:4- and 2:6-dinitrotoluene, from which crystals solidifying at 66—67° can be separated, whereas by the nitration of mononitrotoluene to dinitrotoluene, a mixture solidifying at about 59° is obtained. In like manner, differences may be observed in the products obtained by nitrating toluene to trinitrotoluene directly or in three stages. C. A. M.

The Electrochemical Oxidation of *p*-Nitrotoluene and of its Isomerides. FR. FICHTER and GÉRALD BONHÔTE (*Helv. Chim. Acta*, 1920, 3, 395—409).—Contrary to the statement of Elbs that the electrochemical oxidation of *p*-nitrotoluene does not proceed beyond the formation of *p*-nitrobenzyl alcohol (A., 1897, i, 332), it is shown that under varying conditions in acetic-sulphuric acid solution with a platinum anode, both *p*-nitrobenzaldehyde and *p*-nitrobenzoic acid are produced (compare Coehn, *Zeitsch. Elektrochem.*, 1903, 9, 643; Labhardt and Zschoche, A., 1902, i, 289). The alcohol owes its protection from further oxidation to the simultaneous formation of a tarry product, of low nitrogen content and phenolic in character, together with nitric acid as a result of the replacement of the nitro-group of *p*-nitrotoluene by hydroxyl. In virtue of its easy oxidisability (compare A., 1914, i, 946), this product acts as a depolariser. The acetic acid also plays a part by protecting the alcohol from the action of the nitric acid; if aqueous sulphuric acid be used, a better yield of *p*-nitrobenzoic acid is produced, and *p*-nitrobenzyl alcohol can only be isolated with difficulty. Experiments on the electrolytic oxidation

of phenol showed that the formation of carbon dioxide was greatly increased by nitric acid, but this effect was negligible when acetic acid was also present. Successively better yields of *p*-nitrobenzoic acid, without the formation of tar, are obtained by replacing *p*-nitrotoluene by *p*-nitrobenzyl alcohol or *p*-nitrobenzaldehyde, whether acetic acid be present or not. Owing to its greater oxidisability, *o*-nitrotoluene suffers complete decomposition in aqueous sulphuric acid, but in acetic-sulphuric acid gives a smaller yield of nitrobenzyl alcohol than the para-isomeride (compare Pierron, A., 1901, i, 685), with some tar, whilst the alcohol and the aldehyde may be respectively oxidised in good yield to the aldehyde and the acid. By oxidation in presence of dilute sulphuric acid, *m*-nitrotoluene also suffers complete decomposition, but *m*-nitrobenzyl alcohol cannot be detected among its oxidation products in acetic-sulphuric acid solution, since, like toluene, it yields the aldehyde, or, with sufficient current density, the acid. This may also easily be obtained in good yield from the alcohol and the aldehyde. In explanation of this difference from the ortho- and para-isomerides, it is shown that, of the series *p*-nitrotoluene, *p*-nitrobenzyl alcohol, *p*-nitrobenzaldehyde, and *p*-nitrobenzoic acid, the alcohol shows the maximum polarisation value in presence both of aqueous- and of acetic-sulphuric acids, and, in consequence, it is suggested that a peroxide of *p*-nitrobenzyl alcohol is formed which increases the oxidising effect of the anode on the higher oxidation products. If platinum be replaced by lead peroxide as anode, the alcohol is no longer obtained. When the alcohol is used as starting material, it reacts with any peroxide to form the aldehyde, and so weakens its protective action. The polarisation values of *o*- and *m*-nitrobenzyl alcohols are very small, in accordance with the smaller yields obtained of these substances.

J. K.

Formation and Decomposition of Aromatic Sulphonic Acids by Electrochemical Oxidation. FR. FICHTER, ROBERT BRÄNDLIN, and ERNST R. HALLAUER (*Helv. Chim. Acta*, 1920, 3, 410—422. Compare A., 1914, i, 811).—By electrolytic oxidation of ammonium 4:4'-disulphodiphenyl disulphide at a platinum anode, benzene-*p*-disulphonic acid is produced in 88% yield, but is only freed with difficulty from impurities, presumed to arise from its oxidation (compare Tonoli, *Chem. Zeit.*, 1912, 36, 939). Experiments on the electrolytic oxidation of ammonium benzene-*p*-disulphonate itself indicated the formation of a phenolic compound as intermediate product, the final product being isolated as a barium salt, to which the formula $C_{12}H_6O_{16}S_3Ba_4$ is assigned with reserve. Phenol-2:5-disulphonic acid is probably an intermediate product, since on oxidation it exhibits a similar series of colour changes, probably involving the formation of catechol-4-sulphonic acid. Benzene-*m*-disulphonic acid also appears to furnish phenolic compounds (possibly catechol-4-sulphonic acid and quinolsulphonic acid), since the odour of *p*-benzoquinone is observed and the solution gives a green coloration with ferric chloride, but suffers com-

plete decomposition without offering the possibility of isolating intermediate products.
J. K.

Purification of Decahydronaphthalene TETRALIN G.M.B.H. (D.R.-P. 310781; from *Chem. Zentr.*, 1920, ii, 601—602).—Incompletely hydrogenated naphthalene is treated with liquid sulphur dioxide; naphthalene and its tetra-, hexa-, and octa-hydrated derivatives readily pass into solution, whilst decahydronaphthalene is practically insoluble in this medium.
H. W.

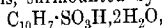
Preparation of Chlorinated Nitronaphthalenes. OSKAR MATTER (D.R.-P. 317755; from *Chem. Zentr.*, 1920, ii, 601).—The chloro-additive compounds of naphthalene are treated with nitric acid at a low temperature, and the products so formed are heated with water or with reagents which combine with acids. Thus, naphthalene dichloride and nitric acid (D 1·5) yield a *nitronaphthalene dichloride* which, when boiled with water or heated with milk of lime, passes into 8-chloro- α -nitronaphthalene, m. p. 93—94°; the latter is reduced by stannous chloride and hydrochloric acid to 8-chloro- α -naphthylamine, m. p. 88—89°. Similarly, naphthalene tetrachloride and nitric acid (D 1·5) form a resinous *nitronaphthalene tetrachloride*, which is transformed by methyl alcohol and sodium carbonate, or by benzene, methyl alcohol, and sodium hydrogen carbonate at 140—150°, into 5:8-dichloro- α -nitronaphthalene, m. p. 94°. 5:8-Dichloro- α -naphthylamine, m. p. 104—105°, is prepared by reducing the latter with tin and hydrochloric acid.
H. W.

The Reduction of Nitronaphthalenesulphonic Acids. HANS EDUARD FIERZ and PAUL WEISSENBACH (*Helv. Chim. Acta*, 1920, 3, 305—311).—The results of previous investigators have tended to show complete agreement between the nitro-derivatives of benzene and of naphthalene in their behaviour on reduction. It is now found that the reduction, whether electrolytic or by means of iron and ferrous sulphate, of 5-nitro- and 8-nitronaphthalene-2-sulphonic acid only yields the corresponding hydroxylamines (compare D.R.-P. 81621). The resulting solutions have strong reducing properties, and give red precipitates of unstable Schiff's bases when treated with formaldehyde and dimethylaniline. Complete reduction is only achieved in weakly acid solution, for example, by the use of ferrous acetate. The 5- and 8-nitronaphthalene-1-sulphonic acids, however, and also 8-nitronaphthalene-1:3:6-trisulphonic acid, may be reduced electrolytically to the amino-acids in 10% sulphuric acid solution, a current density of 200—600 amp./dm.² being employed between lead electrodes.

The dissociation constants of the following acids are given: naphthalene-1-sulphonic acid, 0·18; naphthalene-2-sulphonic acid, 0·25 (compare Wegscheider and Lux, *A.*, 1909, ii, 649); 5-nitronaphthalene-1-sulphonic acid, 0·15, the 8-nitro-isomeride, 0·094;

5-nitronaphthalene-2-sulphonic acid, 0·10, the 8-nitro-isomeride, 0·13; 8-nitronaphthalene-1:3:6-trisulphonic acid, 0·055. J. K.

Naphthalene-1-sulphonic Acid. HANS EDUARD FIERZ and PAUL WEISSENBACH (*Helv. Chim. Acta*, 1920, **3**, 312—318).—It is shown that the sulphonation of naphthalene, even at low temperatures, always results in the formation of some naphthalene-2-sulphonic acid, for example, at least 2% at 0° (Euwe, A., 1909, i, 707). The determination of the proportion is based on the fact that the 1-acid crystallises from aqueous solution as a dihydrate, whilst the 2-acid forms a trihydrate. Apparently the process of sulphonation consists in the formation of a molecular compound, which undergoes decomposition into either the 1- or the 2-acid, according to the prevailing external conditions. Naphthalene-1-sulphonic acid separates from aqueous solution in the form of tiny, non-deliquescent columns, surmounted by pyramids,



m. p. 90°, which cannot be completely dehydrated without decomposition. The ammonium salt, $\text{C}_{10}\text{H}_7\cdot\text{SO}_3\cdot\text{NH}_4$, pearly leaflets; the lead salt, $(\text{C}_{10}\text{H}_7\cdot\text{SO}_3)_2\cdot\text{Pb}\cdot 3\text{H}_2\text{O}$, lustrous leaflets, is converted into the monohydrate at 85°; the zinc salt ($6\text{H}_2\text{O}$), thin leaflets; the cobalt salt ($6\text{H}_2\text{O}$), lustrous, pale red leaflets, is bluish-violet when anhydrous; the nickel salt ($6\text{H}_2\text{O}$), lustrous, light green leaflets, turns yellow and becomes anhydrous at 185°; the copper salt ($6\text{H}_2\text{O}$), turquoise-blue leaflets, is dehydrated and turned yellow at 180°; the cadmium salt ($6\text{H}_2\text{O}$) and the zinc salt ($6\text{H}_2\text{O}$) form leaflets. The strontium salt crystallises as a dihydrate. J. K.

Action of Aqueous Sodium Hydroxide on the α -Naphthylaminesulphonic Acids. HANS EDUARD FIERZ (*Helv. Chim. Acta*, 1920, **3**, 318—329).—Diagrams of curves are given expressing the tabulated results of a quantitative study of the proportions of the products obtained by the treatment of the α -naphthylaminesulphonic acids with varying strengths of sodium hydroxide solution at different temperatures. The following products are obtained, the figures in brackets indicating the maximum proportion observed, with the corresponding temperature and strength of alkali employed, time of action in all cases being three hours; from α -naphthylamine-4-sulphonic acid: α -naphthol (59%), α -naphthol-4-sulphonic acid (54%; 280°, 10%), 1:4-dihydroxynaphthalene (traces), but no α -naphthylamine; from α -naphthylamine-5-sulphonic acid, 1:5-dihydroxynaphthalene (60·2%; 290°, 30 or 50%), 5-amino- α -naphthol (52·4%; 250°, 30%), α -naphthylamine (7·8%; 300°, 50%), and probably a little α -naphthol-5-sulphonic acid; from α -naphthylamine-6-sulphonic acid, α -naphthol-5 (1)-sulphonic acid (49%; 260°, 20%), 1:6-dihydroxynaphthalene (17%; 260°, 50%), α -naphthylamine (0·3%; 260°, 20 or 50%), unchanged acid (37%; 260°, 20%) and traces of 5-amino- β -naphthol; from α -naphthylamine-7-sulphonic acid, α -naphthol-7-sulphonic acid (40%[!]; 260°, 50%), 8-amino- β -naphthol (37·7%; 260°, 50%), 1:7-dihydroxynaphthalene (3%; 260°, 20%), unchanged acid (55%;

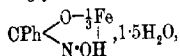
260°, 20%); from α -naphthylamine-8-sulphonic acid, 1:8-dihydroxy-naphthalene (46.6% [70% by very rapid heating]; 300°, 10%), α -naphthylamine (32.5%), α -naphthol-8-sulphonic acid, and traces of 8-amino- α -naphthol. Some naphthalene is always produced when naphthalene-1- or -2-sulphonic acids are fused with sodium hydroxide solution (compare Willson and Meyer, A., 1915, i, 232).

J. K.

Preparation of Hexanitrodiphenylamine and its Use as a Primer in Shell Charges. JOHN MARSHALL (*J. Ind. Eng. Chem.*, 1920, 12, 336—340).—Hexanitrodiphenylamine is more stable than tetranitromethylaniline or tetranitroaniline, and is superior to trinitrotoluene as a detonator. It may be prepared on a large scale by a modification of Carter's method (*Zeitsch. ges. Schiess. u. Sprengstoffw.*, 1913, 205) of nitrating aniline. In the first stage, two mols. of aniline and one mol. of chloronitrobenzene are emulsified with hot water, and the temperature raised to 80° for an hour. Dinitrodiphenylamine is precipitated in clusters of red needles melting at 148° to 152°. This is converted into tetranitrodiphenylamine by nitration with a suitable mixture of nitric and sulphuric acids, first at 70° and then at 80° to 90°, yielding a brownish-yellow, amorphous mass containing small amounts of higher nitration products. The final nitration of this material is effected at 90°, and yields up to 80% of the theoretical amount of hexanitrodiphenylamine in yellow crystals melting at 238.5—239.5°. The method of nitrating dinitrodiphenylamine in one operation, suggested by Hoffmann and Dame (A., 1919, i, 394), is less suitable, since it yields an amorphous material melting at 238°. The absolute density of the crystalline product was 1.653. [See, further, *J. Soc. Chem. Ind.*, 1920, 429A.] C. A. M.

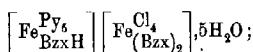
Preparation of Diarylurethanes. CHEMISCHE FABRIKEN VORN WEILER TER MEER (D.R.-P. 306316; from *Chem. Zentr.*, 1920, ii, 491—492).—The diarylamine or its hydrochloride (one molecule) is warmed with one or more molecules of ethyl chloroformate in the presence or absence of a solvent until hydrogen chloride ceases to be evolved. When only one molecule of diarylamine is employed, a quantitative conversion of diarylamine into urethane is effected, and free hydrogen chloride is evolved. The preparation of diphenylurethane from diphenylamine and chloroformic ester is particularly described. H. W.

Ferribenzhydroxamic Acid Compounds. R. F. WEINLAND and GERTRUD BAIER (*Ber.*, 1920, 53, [B], 685—696).—Addition of aqueous ferric chloride to a solution of sodium benzhydroxamate in water yields the sparingly soluble ferribenzhydroxamate,



reddish-brown rods or six-sided platelets from 96% alcohol, needles from more dilute alcohol. The substance behaves as an internally

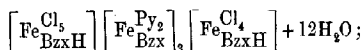
complex salt; it dissolves readily in aqueous solutions of all types of bases and in dilute acids, apparently with formation of salts, which can only exist in solution, since the latter ultimately deposits the original material. From alcoholic solutions of ferric chloride, benzhydroxamic acid and pyridine (or quinoline), the following series of salts has been prepared [in the formulation of which BzxH represents the benzhydroxamic acid molecule and Bzx the radicle $\text{PhC}(\text{N}\cdot\text{OH})\cdot\text{O}$]: (i) rectangular, violet platelets,



(ii) pale violet, irregular, six-sided platelets, $\left[\text{Fe} \begin{smallmatrix} \text{Py}_5 \\ \text{Bzx} \end{smallmatrix} \right] \left[\text{Fe} \begin{smallmatrix} \text{Cl}_4 \\ \text{Bzx} \\ \text{Py} \end{smallmatrix} \right]$,

which are converted by water into ferribenzhydroxamate; (iii) the cherry-red salts $\text{FeCl}_3\cdot\text{BzxHPy}$ and $\text{FeCl}_3\cdot\text{BzxH}$ Quinoline, which are soluble in water and are to be regarded simply as the pyridine and quinoline salts of a trichlorobenzhydroxamatoferri-acid,

$\left[\text{Fe} \begin{smallmatrix} \text{Cl}_3 \\ \text{Bzx} \end{smallmatrix} \right] \text{H}$; (iv) dark red, shining powder,



(v) dark red salt, $[\text{FeCl}_3] \left[\text{Fe} \begin{smallmatrix} \text{Quinoline}_2 \\ \text{Bzx}_2 \end{smallmatrix} \right]_3 \left[\text{Fe} \begin{smallmatrix} \text{Cl}_4 \\ \text{BzxH} \end{smallmatrix} \right] + 6\text{H}_2\text{O}$;

(vi) reddish-brown needles, $2 \left[\text{Fe} \begin{smallmatrix} \text{Py} \\ \text{Cl} \\ \text{Bzx}_2 \end{smallmatrix} \right] \left[\text{Fe} \begin{smallmatrix} \text{Py} \\ \text{Bzx}_2 \end{smallmatrix} \right] + 6\text{H}_2\text{O}$. The

preparation of the individual salts is effected by suitably varying the relative proportions of the components; for details, the original must be consulted. H. W.

Preparation of Dinitrophenol. OSWALD SILBERRAD (Brit. Pat. 140955).—2:4-Dinitrophenol is obtained by suspending 100 parts of *p*-nitrosophenol in a solution of 200 parts of sodium nitrate in 350 parts of water and running the mixture into 480 parts of 50% sulphuric acid at 70–80°, the temperature being finally raised to, and maintained for six hours at, 95°. The yield amounts to 135 parts of dinitrophenol, representing 130% on the phenol initially employed. If desired, nitric acid (D 1:2) may be substituted for the sodium nitrate and sulphuric acid. G. F. M.

Preparation of Pyrogallol. NITRITFABRIK AKT.-GES. (Brit. Pat. 140694).—Pyrogallol is obtained in nearly theoretical yield by heating solutions or suspensions of tannic or gallic acids at temperatures above 160° in an autoclave, with a proportion of alkali or alkaline earth, etc., hydroxides or carbonates not materially exceeding twice the amount required to effect substitution of the hydrogen atoms of the carboxyl groups initially present and those formed by hydrolysis, if any. G. F. M.

The Valency Problem of Sulphur. III. H. LECHER (*Ber.*, 1920, **53**, [B], 577—590. Compare A., 1915, i, 532; 1916, i, 41).—In previous communications (A., 1915, i, 532; 1916, i, 41), evidence has been brought forward to show that diphenyl disulphide and di-*p*-dimethylaminodiphenyl disulphide are not appreciably dissociated into free radicals, since their solutions obey Beer's law. This method of attacking the problem is not, however, sufficiently accurate to enable conclusions to be drawn as to the possibility of a slight dissociation. A different mode of working has now been adopted, and it is shown that a solution of molar amounts of diphenyl disulphide and di-*o*-nitrodiphenyl disulphide in boiling xylene is unchanged after three hours, and in benzene at 200° is unaltered after six hours, and that the same is true of equivalent solutions of *o*-nitrodiphenyl disulphide in the same solvents. From these experiments, the conclusion is drawn that the solutions of the latter substance cannot contain any free radicle, and, whilst a partial dissociation of one of the symmetrical disulphides is not absolutely excluded, it is highly improbable that such is actually the case.

Diphenyl disulphide, di-*p*-dimethylaminodiphenyl disulphide, di-*o*-nitrodiphenyl disulphide, and *o*-nitrodiphenyl disulphide exhibit thermochromic properties, darkening when heated in the crystalline or molten condition or when in solution, and returning to their original colour when cooled. The phenomenon is exhibited most strongly by the dimethylamino-, least strongly by the nitro-derivatives. It does not appear to depend on the formation of free radicals, and is not a specific property of the disulphide group, since it is also exhibited by *o*-nitrodiphenyl sulphide. It may possibly be partly attributable to the presence of the nitro-group, since nitrobenzene is itself thermochromic.

The dissociation of mercury phenylmercaptide into mercury and diphenyl disulphide, $\text{Hg}(\text{SPh})_2 = \text{Hg} + \text{PhS} \cdot \text{SPh}$, does not appear to be attributable to a preliminary detachment of the SPh-radicle, since *o*-nitrodiphenyl disulphide is found to react with mercury under conditions which preclude the presence of the free radicle; the products of the action are diphenyl disulphide, di-*o*-nitrodiphenyl disulphide, and mercury *o*-nitrophenylmercaptide, small, yellow, very electric needles, m. p. 231° (decomp.) after softening at 222° and darkening at 228°.

o-Nitrodiphenyl disulphide, $\text{NO}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{S} \cdot \text{SPh}$, long, yellow crystals, m. p. 55°, is smoothly prepared by the action of *o*-nitrochloroethiolbenzene (Zincke and Farr, A., 1912, i, 763) on phenylmercaptan in dry ethereal solution. H. W.

Reduction of Organic Disulphides by Alkali Mercaptides.

H. LECHER (*Ber.*, 1920, **53**, [B], 591—593).—The author has attempted to prepare *o*-nitrodiphenyl disulphide, $\text{NO}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{S} \cdot \text{SPh}$, by the action of *o*-nitrochloroethiolbenzene (Zincke and Farr, A., 1912, i, 763) on sodium phenyl sulphide, but has thereby obtained

mainly a mixture of the *s*-diphenyl disulphide and di-*o*-nitro-diphenyl disulphide. The *as*-disulphide is shown to be formed primarily and to be immediately reduced by the sodium phenyl sulphide to diphenyl disulphide and sodium *o*-nitrophenyl mercaptide, $\text{NO}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{S} \cdot \text{SPh} + \text{PhSNa} = \text{NO}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{SNa} + \text{PhS} \cdot \text{SPh}$; the latter then reacts with $\frac{1}{2}$ *o*-nitrochlorothiobenzene to yield di-*o*-nitrodiphenyl disulphide. H. W.

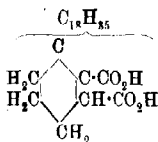
Cholesterol. XXIX. Certain Derivatives of Cholestene and ψ -Cholestene and the Proof of the Existence of a Methylene Group adjacent to a Double Bond in Cholesterol. A. WINDAUS (*Ber.*, 1920, **53**, [B], 488–497).—Cholestene and ψ -cholestene have been converted into three different monoketones,



in which the carbonyl group is in the positions 6, 7, and 8 respectively when the numbering shown in the annexed scheme is adopted.

Nitrocholestene, leaflets, m. p. 117–118° (Mauthner and Suida give m. p. 105°), is prepared in 75% yield by the action of fuming nitric acid (D 1.52) on a solution of cholestene in glacial acetic acid, and is converted by potassium cyanide into *nitrocholestene hydrocyanide*, long needles, m. p. 162°, from which cholestan-7-one, m. p. 98–99°, is prepared, which is identical with heterocholestanone described by Windaus and Dalmer (*A.*, 1919, i, 204). The latter, when oxidised by chromic acid in hot glacial acetic acid solution, yields an acid product which shows no tendency to crystallise, but which, on distillation under diminished pressure, gives an unsaturated hydrocarbon, $\text{C}_{25}\text{H}_{42}$ or $\text{C}_{25}\text{H}_{44}$ [identical with the product obtained by Windaus and Resan (*A.*, 1914, i, 682) by the oxidation of cholestene with permanganate], transformable by catalytic hydrogenation into a saturated hydrocarbon, m. p. 45° (see later). Similarly, 4-chlorocholestane-7-one is converted by chromic acid into a non-crystalline acid, from which an unsaturated hydrocarbon, $\text{C}_{25}\text{H}_{40}$ or $\text{C}_{25}\text{H}_{42}$, m. p. 76°, is obtained, identical with the product isolated by Windaus and Resan (*loc. cit.*) by the distillation of the acidic oxidation compounds of cholesteryl acetate. Catalytic hydrogenation in ethereal solution converts the latter mainly into a saturated hydrocarbon, m. p. 80°, whilst in glacial acetic acid solution the hydrocarbon, m. p. 45° (see above), is formed.

Nitro- ψ -cholestene, $\text{C}_{27}\text{H}_{45}\text{O}_2\text{N}$, has m. p. 70°, and is converted by zinc dust and acetic acid into *cholestan-6-one*, m. p. 98–99° (*oxime*, slender needles, m. p. 205°). The latter is reduced by amalgamated zinc and hydrochloric acid to cholestan, m. p. 79–80°, and is oxidised by fuming nitric acid to a dicarboxylic acid (annexed formula), m. p. 240°.



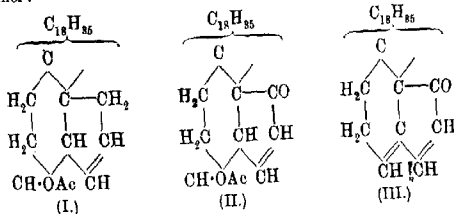
The oxidation of cholestene by a considerable excess of chromic acid in glacial acetic acid solution leads to the production of small

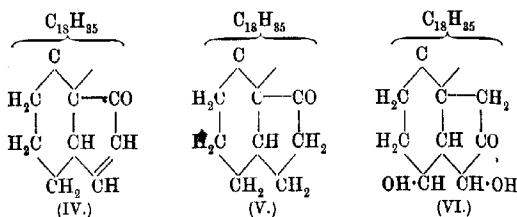
amounts (ca. 10%) of the unsaturated ketone, *ketocholestene* (annexed formula), plate-like crystals, m. p. 145° (*semicarbazone*, small needles, m. p. 225° [decomp.]). The constitution of the latter follows from its catalytic hydrogenation to *cholestane-8-one*, m. p. $108-109^{\circ}$, which is found to differ from either *cholestane-6-* or *-7-one*, but to be oxidised by fuming nitric acid to a dicarboxylic acid, $C_{27}H_{46}O_4$, identical with that obtained from *cholestane-7-one*, thus showing the keto-group to be present in the position 8. Hence, *cholestene* must contain the methylene group in juxtaposition to the group $-CH:CH-$, and this arrangement must also be present in the cholesterol molecule.

H. W.

Cholesterol. XXX. Oxidation of Cholesteryl Acetate. A. WINDAUS and E. KIRCHNER (*Ber.*, 1920, **53**, [B], 614-621).—The oxidation of cholesteryl acetate (I) with chromic acid (Mauthner and Suida, A., 1897, i, 31; Windaus and Resau, A., 1915, i, 677) yields a mixture of β -oxycholesteryl acetate and a substance, $C_{29}H_{48}O_4$, the constitutions of which have not been satisfactorily elucidated. Attempts have been made in this direction by Windaus and Resau (*loc. cit.*), but their arguments are based on a formula for cholesterol since disproved. Revision of the latter (preceding abstract) has enabled the problem to be solved.

β -Oxycholesteryl acetate (II) is readily hydrolysed to the simply unsaturated keto-alcohol oxycholestenol, which readily loses water and yields the doubly unsaturated ketone, *ketocholesterylene* (III). The latter, when submitted to step-wise catalytic hydrogenation, first absorbs two atoms of hydrogen, and gives the previously described *ketocholestene* (IV), and then reacts with a further two atoms to yield *cholestane-8-one* (V) (*loc. cit.*). The same product is ultimately obtained when ψ -cholesterol (obtained from *ketocholesterylene* by means of sodium and alcohol) is first oxidised to the unsaturated ketone, ψ -cholestenone, and then catalytically hydrogenated. The oxidation of cholesteryl acetate is therefore precisely analogous to that of *cholestene*, the methylene group adjacent to the double bond being converted into the keto-group. The individual products are therefore formulated in the following manner:





It is further shown that β -oxycholestenyl acetate can be reduced by hydrogen in the presence of spongy palladium to *ketocholestenyl acetate*, needles, m. p. 142—143°, which, on hydrolysis, yields *cholestane-8-one-4-ol*, pearly leaflets, m. p. 156—157°; the latter is oxidised by chromic acid in the presence of acetic acid to *cholestane-4:8-dione*, needles, m. p. 186—187°, the *dioxime* of which has m. p. 281° (decomp.).

The substance, $C_{29}H_{48}O_4$, is the monoacetyl derivative of a cholestane-one-diol, which is now shown to be *isocholestane-7-one-4:5-diol* (VI), since, when cautiously oxidised, it passes into the previously described *isocholestane-4:7-dione-6-ol*, which is successively convertible into *cholestene-4:7-dione* and *cholestane-4:7-dione*. H. W.

Syntheses with the Aid of Monochloromethyl Ether. IV. The Condensation of Ethyl Benzylsodiummalonate and Monochloromethyl Ether. JOHN LIONEL SIMONSEN (T., 1920, 117, 564—569).

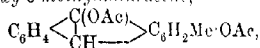
The Preparation of *cyclo*Heptane-1 : 1-diacetic Acid.
JAMES NELSON EDMUND DAY, GEORGE ARMAND ROBERT KON, and
ARNOLD STEVENSON (T., 1920, **117**, 639—646).

Derivatives of α -Arylphthalides and their Conversion into Anthracene Derivatives. A. BISTRZYCKI and S. ZEN-RUFFINEN (*Helv. Chim. Acta*, 1920, **3**, 369—391. Compare A., 1899, i, 151).

—6-Hydroxy-*m*-tolylphthalide, $\text{CO} \begin{array}{c} \diagup \text{O} \diagdown \\ \text{C}_6\text{H}_4 \end{array} \text{CH} \cdot \text{C}_6\text{H}_3\text{Me} \cdot \text{OH}$,
m. p. 164.5–165.5° (Winkler, *Diss.*, Freiburg [Switzerland], 1901)
is best prepared by the condensation of *o*-phthalaldehydic acid with
o-cresol in presence of 73% sulphuric acid; it yields a *benzoyl* deriva-
tive, $\text{C}_{22}\text{H}_{16}\text{O}_4$, m. p. 123–124°; ethylation gives its *ethyl ether*,
 $\text{C}_{17}\text{H}_{16}\text{O}_3$, m. p. 96.5–97.5°; its *methyl ether*, $\text{C}_{16}\text{H}_{14}\text{O}_3$, m. p.
124.5–125.5°, is formed from *o*-phthalaldehydic acid and *o*-tolyl
methyl ether; its 5'-*bromo*-derivative, $\text{C}_{15}\text{H}_{11}\text{O}_3\text{Br}$, m. p. 185–186°,
gives an *acetyl* derivative, $\text{C}_{17}\text{H}_{13}\text{O}_3\text{Br}$, m. p. 131–132°; its 5'-*nitro*-
derivative, $\text{C}_{15}\text{H}_{11}\text{O}_3\text{N}$, has m. p. 182°. 6'-*Hydroxyphenyl m*-tolyl-
methane-2-carboxylic acid, $\text{OH} \cdot \text{C}_6\text{H}_3\text{Me} \cdot \text{CH}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{CO}_2\text{H}$, m.
p. 215–216° (silver salt, $\text{C}_{15}\text{H}_{13}\text{O}_3\text{Ag}$), obtained from the above
phthalide by reduction with zinc dust and sodium hydroxide, is

converted by cold sulphuric acid into 2-hydroxy-3-methyl-9-anthrone, $\text{C}_6\text{H}_4 \begin{smallmatrix} \text{CO} \\ \text{CH}_2 \end{smallmatrix} \text{C}_6\text{H}_2\text{Me}\cdot\text{OH}$, glistening prisms, m. p.

276—277°, which does not fluoresce in solution. It dissolves in cold potassium hydroxide solution, and by saturating the solution at 0° with carbon dioxide, a yellow precipitate, probably of the isomeric anthranol, is produced. By acetylation, the anthrone yields 2:9-diacetoxy-3-methylantracene,

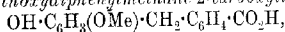


leaflets, m. p. 171—172°, which shows a blue fluorescence in acetic acid solution, and on oxidation with chromic acid gives 2-acetoxy-3-methylanthraquinone, $\text{C}_6\text{H}_4 \begin{smallmatrix} \text{CO} \\ \text{CO} \end{smallmatrix} \text{C}_6\text{H}_2\text{Me}\cdot\text{OAc}$, needles, m. p.

177°, from which 3-hydroxy-2-methylanthraquinone, m. p. 298·5° (Fraude, 1879), is obtained by hydrolysis. 3-*p*-Hydroxy-*m*-

methoxyphenylphthalide, $\text{CO} \begin{smallmatrix} \text{O} \\ \text{C}_6\text{H}_4 \end{smallmatrix} \text{CH}\cdot\text{C}_6\text{H}_3 \begin{smallmatrix} \text{OH} \\ \text{OMe} \end{smallmatrix}$, m. p.

110·5—112·5°, from *o*-phthalaldehydic acid and guaiacol, gives an acetyl derivative, $\text{C}_{17}\text{H}_{14}\text{O}_5$, m. p. 142—143°, and, by reduction, 4'-hydroxy-3'-methoxydiphenylmethane-2-carboxylic acid,

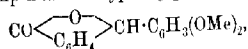


m. p. 150—151° (silver salt, $\text{C}_{15}\text{H}_{13}\text{O}_4\text{Ag}$). 2-Hydroxy-3-methoxy-9-anthrone, $\text{C}_6\text{H}_4 \begin{smallmatrix} \text{CO} \\ \text{CH}_2 \end{smallmatrix} \text{C}_6\text{H}_2 \begin{smallmatrix} \text{OH} \\ \text{OMe} \end{smallmatrix}$, m. p. 211—213°, from the

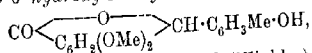
acid just mentioned, shows no fluorescence in solution, but dissolves in cold potassium hydroxide solution, and, on acetylation, gives

2:9-diacetoxy-3-methoxyanthracene, $\text{C}_6\text{H}_4 \begin{smallmatrix} \text{C(OAc)} \\ \text{CH} \end{smallmatrix} \text{C}_6\text{H}_2 \begin{smallmatrix} \text{OAc} \\ \text{OMe} \end{smallmatrix}$

m. p. 158·5—160·5°, from which 2-acetoxy-3-methoxyanthraquinone, $\text{C}_6\text{H}_4 \begin{smallmatrix} \text{CO} \\ \text{CO} \end{smallmatrix} \text{C}_6\text{H}_2 \begin{smallmatrix} \text{OAc} \\ \text{OMe} \end{smallmatrix}$, m. p. 200·5—201·5°, is obtained by oxidation. This compound furnishes hystazarin monomethyl ether on hydrolysis. 3-*mp*-Dimethoxyphenylphthalide,



m. p. 144—145°, from *o*-phthalaldehydic acid and veratrole, suffers rupture of the lactonic ring when boiled in alcoholic solution with potassium hydroxide, and the resulting solution, on oxidation with potassium permanganate, gives *o*-3':4'-dimethoxybenzoylbenzoic acid (Lagodzinski, A., 1905, i, 82). By reduction of the phthalide, only a small quantity of the expected dimethoxydiphenylmethane-carboxylic acid is produced. The condensation of opianic acid with *o*-cresol to 6'-hydroxy-*m*-tolylmeconine,



m. p. 181°, acetyl derivative, m. p. 137° (Winkler), is best carried out in presence of sulphuric acid; its methyl ether, $\text{C}_{18}\text{H}_{18}\text{O}_5$, m. p. 117·5—119°, may be obtained by methylation or from opianic

acid and *o*-tolyl methyl ether, and when boiled with dilute potassium hydroxide solution undergoes to a slight extent rupture of the lactonic ring. Neither the parent compound nor its methyl ether could be converted into a diphenylmethanecarboxylic acid by reduction. This was also the case with 3-*p*-hydroxy-*m*-methoxy-*meconine*, $\text{CO} \begin{array}{c} \diagup \text{O} \diagdown \\ \text{C}_6\text{H}_4(\text{OMe})_2 \end{array} \text{CH} \cdot \text{C}_6\text{H}_5 \begin{array}{c} \diagup \text{OMe} \diagdown \\ \text{OH} \end{array}$, m. p. 164–166°; 3-*mp*-dimethoxyphenylmeconine, m. p. 120.5–121.5°, yields tetramethoxy-*o*-benzoylbenzoic acid (Bentley and Weizmann, T., 1908, 93, 437) on oxidation; 3-*oreylmeconine*,

$\text{CO} \begin{array}{c} \diagup \text{O} \diagdown \\ \text{C}_6\text{H}_4(\text{OMe})_2 \end{array} \text{CH} \cdot \text{C}_6\text{H}_2\text{Me}(\text{OH})_2$,
m. p. 223–225°; 3-*p*-dimethylaminophenylmeconine,

$\text{CO} \begin{array}{c} \diagup \text{O} \diagdown \\ \text{C}_6\text{H}_4(\text{OMe})_2 \end{array} \text{CH} \cdot \text{C}_6\text{H}_4 \cdot \text{NMe}_2$,
m. p. 132.5–134.5° (hydrochloride, needles), from opianic acid and dimethylaniline in presence of anhydrous oxalic acid, can also not be reduced by zinc dust and sodium hydroxide. Bistrzycki's 2-hydroxyanthranol (A., 1899, i, 151) is really 2-hydroxy-9-anthrone, $\text{C}_6\text{H}_4 \begin{array}{c} \diagup \text{CO} \diagdown \\ \text{CH}_2 \end{array} \text{C}_6\text{H}_3 \cdot \text{OH}$, and, similarly, 2:3':4'-trimethoxydihydroanthrone is 3:4:7-trimethoxy-9-anthrone. 3-(*Nitro-β*-hydrozynaphthyl)-phthalide, $\text{CO} \begin{array}{c} \diagup \text{O} \diagdown \\ \text{C}_6\text{H}_4 \end{array} \text{CH} \cdot \text{C}_{10}\text{H}_7 \begin{array}{c} \diagup \text{NO}_2 \diagdown \\ \text{OH} \end{array}$, decomp. at 130.5°, is obtained by nitrating β-hydrozynaphthylphthalide.
J. K.

Truxillic Acids. II. R. STOERMER and E. EMMEL (*Ber.*, 1920, 53, [B], 497–508. Compare Stoermer and Foerster, A., 1919, i, 444).—Further investigation of ε-truxillic acid leads the authors to the conclusion that it is an unusually stable *trans*-acid (annexed formula), the view being maintained that the truxillic acids and the *isotruxillic* acid are structural and not stereo-isomerides.

ε-Truxillic acid, long, colourless needles, m. p. 192° (identical with Hesse's β-cocaine acid), is conveniently prepared by protracted heating of α-truxillic acid with alkali hydroxide. It is not affected by prolonged heating or by drastic treatment with hydrochloric acid. Attempts to convert it into an internal anhydride were unsuccessful, but, by the action of acetic anhydride on the acid at 200–210°, or of phosphoryl chloride on the potassium salt, a non-crystalline anhydride of high molecular weight is obtained, which, however, is reconverted by water into ε-truxillic acid. The nature of the product is confirmed by its conversion by ethyl alcohol into *ethyl hydrogen ε-truxillate*, and by aniline into ε-truxillid*anilide*, m. p. 284°, and ε-truxill*anilic acid*, needles, m. p. 293°.

The following derivatives of ε-truxillic acid are described: the *barium* and *calcium* salts, which are less soluble in hot than in cold water; methyl ester, m. p. 64°; *ethyl ester*, m. p. 34°; *chloride*,

m. p. 106—107°; *diamide*, small, transparent needles, m. p. 240°; *tetramethyldiamide*, m. p. 190°; *dianilide*, slender, silky needles, m. p. 284°.

The following investigations have been carried out in connexion with attempts to convert the truxillic acids into *cyclobutanetetra-carboxylic acids* (*loc. cit.*), but success has not been thus far achieved. Dinitro- γ -truxillic acid, m. p. 293°, is most conveniently obtained by the action of fuming nitric acid (D 1.5) on the γ -anhydride, and is converted by acetic anhydride into dinitro- γ -truxillic anhydride, small prisms, m. p. 229°. The acid is converted in the usual manner into *methyl dinitro- γ -truxillate*, silky needles, m. p. 194°, *ethyl dinitro- γ -truxillate*, glassy needles, m. p. 146°, and *dinitro- γ -truxillyl chloride*, yellow prisms, m. p. 204°. The latter readily yields the corresponding *diamide*, pale yellow crystals, m. p. 280°, *tetramethyldiamide*, m. p. 276°, and *dianilide*, m. p. 261°. Dinitro- γ -truxillic anhydride is transformed by aniline, according to conditions, either into *dinitro- γ -truxillanic acid*, m. p. 265°, or the corresponding *dianilide*; in contrast to the behaviour of β -isotruxillic anhydride, it could not be caused to yield an anil or a fluorescein derivative. With ethyl alcohol, it gives *ethyl hydrogen dinitro- γ -truxillate*, long needles, m. p. 176—177°.

Ethyl dinitro- γ -truxillate is reduced by hydrogen in the presence of palladium to *ethyl diamino- γ -truxillate*, m. p. 162—163°; definite substances could not be isolated from the products of the oxidation of the hydrolysed ester by permanganate in acid or alkaline solution.

H. W.

Bis-tropic Acids. JULIUS VON BRAUN and LUDWIG NEUMANN (*Ber.*, 1920, **53**, [B], 594—601).—The experiments were undertaken with the pharmacologically interesting object of determining the extent to which it is possible to introduce doubly the group $-CH(CH_2OH) \cdot CO_2H$, characteristic of tropic acid, into the aromatic nucleus. Unfortunately, the derivatives from *m*-xylene exhibit little tendency to crystallise, and cannot be distilled without decomposition, whilst the crystalline compounds from *o*- and *p*-xylenes could not be prepared on a sufficiently large scale owing to the prevalent scarcity of the parent hydrocarbons.

Ethyl *p*-phenylenediacetate readily condenses with ethyl formate in the presence of sodium and ether to yield *ethyl bishydroxy-methylene-p-phenylenediacetate*, $C_{16}H_{14}[C(CH_2OH) \cdot CO_2Et]_2$, m. p. 112—114°; the substance is immediately and completely soluble in dilute alkali or sodium carbonate solution, and in alcoholic solution gives an immediate, very dark bluish-violet coloration with ferric chloride. It readily yields a pale green, basic *copper salt*, and is transformed by aniline into the corresponding *dianilide*, $C_{16}H_{14}[C(CH_2NHPh) \cdot CO_2Et]_2$, crystalline powder, m. p. 143°. The *benzoyl* derivative has m. p. 186—187°. With phenylcarbimide, the ester yields diphenylcarbamide, owing to the unexpectedly ready elimination of water. Unlike ethyl and methyl formyl-

phenylacetates, the ester appears to have absolutely no tendency to pass into the ketonic form, and this fact appears to afford a certain amount of evidence against the aldo-enolic formulation of the former. An ethereal solution of the *p*-phenylene ester is readily reduced by activated aluminium (yield, 50%) to ethyl *p*-phenylenebistropate [ethyl bis(hydroxymethyl)-*p*-phenylenediacetate], $C_6H_4[CH(CH_2OH)CO_2Et]_2$, m. p. 65–66°, which is hydrolysed by aqueous barium hydroxide to *p*-phenylenebistropic acid, shining leaflets, m. p. 93–94°.

Ethyl *m*-phenylenediacetate, colourless liquid, b. p. 196–198°/14 mm., condenses readily with ethyl formate, yielding a product which gives an intense bluish-violet coloration with ferric chloride, but which could only be obtained as a rather viscous, non-crystallisable oil, which decomposed when distilled even in a cathode vacuum. The reduction product is also an oil, whilst the acid corresponding with it could only be obtained as a sticky mass.

Ethyl diformyl-*o*-phenylenediacetate, prepared in the same manner as, but rather more readily than, the corresponding para-derivative, forms dark yellow crystals, m. p. 77–78°, and behaves solely as an enolic form. It is readily soluble in sodium carbonate, gives an intense bluish-green coloration with ferric chloride, a moss-green copper salt, and a dark yellow anilide, m. p. 200°. Like the para-compound, it loses water and forms diphenylcarbamide when treated with phenylcarbimide. Unlike the para-compound and all other formyl derivatives, however, it gives an intense permanganate-like coloration when its solution in alkali is shaken with benzoyl chloride, and an amorphous, violet precipitate rapidly separates.

H. W.

Formation and Stability of Associated Alicyclic Systems. I. A System of Nomenclature, and some Derivatives of Methane-II-cyclopropane and of Methane-III-cyclopropane. RICHARD MOORE BEESLEY and JOCELYN FIELD THORPE (T., 1920, 117, 591–620).

Preparation of Mellitic Acid. RICHARD LORENZ and JULIUS HAUSMANN (D.R.-P. 318200; from *Chem. Zentr.*, 1920, ii, 492).—Mixtures of finely divided carbon or soot with tar, pressed into rods or plates and subsequently heated in the absence of air, are subjected to anodic oxidation in an alkaline electrolyte; the liberated hydrogen may be obtained as by-product if a diaphragm is used. Soot may be replaced by other finely divided varieties of carbon, such as wood charcoal, lamp-black, or gas carbon, either alone or in admixture with soot. Solutions of sodium or potassium hydroxide, or of alkali carbonates or hydrogen carbonates, may be used as electrolytes.

H. W.

Some Derivatives of 2:4-Dinitrobenzaldehyde. ALEXANDER LOWY and BLAINE B. WESCOTT (*J. Amer. Chem. Soc.*, 1920, 42, 849–856).—A number of condensation products of 2:4-di-

nitrobenzaldehyde with aromatic amines are described. No evidence of stereoisomerism could be observed among them, and attempts to isolate the intermediate additive compounds were unsuccessful.

2:4-Dinitrobenzylidene-m-toluidine, $C_6H_3(NO_2)_2 \cdot CH:N \cdot C_6H_4Me$, yellow needles, m. p. 130° ; 2:4-dinitrobenzylidene-m-4-xylydine, $C_6H_3(NO_2)_2 \cdot CH:N \cdot C_6H_3Me_2$, yellow needles, m. p. 210.5° ; 2:4-dinitrobenzylidene-3-nitro-p-toluidine,

$C_6H_3(NO_2)_3 \cdot CH:N \cdot C_6H_3Me \cdot NO_2$, yellow needles, m. p. 195° ; 2:4-dinitrobenzylidene- ψ -cumidine, $C_6H_3(NO_2)_2 \cdot CH:N \cdot C_6H_3Me_2$, yellow needles, m. p. 186.5° ; sodium 2:4-dinitrobenzylidenesulphanilate,

$C_6H_3(NO_2)_2 \cdot CH:N \cdot C_6H_4 \cdot SO_3Na \cdot H_2O$, pale yellow crystals, decomposing at 249° ; sodium 2:4-dinitrobenzylidenemetanilate ($3H_2O$), yellow needles, decomposing at 185° ; sodium 2:4-dinitrobenzylidenenaphthionate,

$C_6H_3(NO_2)_2 \cdot CH:N \cdot C_{10}H_7 \cdot SO_3Na \cdot \frac{1}{2}H_2O$, orange needles, decomposing at 248° . By condensation with dimethylaniline, 2:4-dinitrobenzaldehyde yields a green dye, doubtless a derivative of malachite-green. J. K.

Constitution of the Methylethylcyclohexanone prepared by Ethylation of 1-Methylcyclohexan-6-one. A. HALLER and R. CORNUBERT (*Compt. rend.*, 1920, **170**, 973-976).—The compound previously prepared by the ethylation of 1-methylcyclohexan-6-one in the presence of sodamide (compare A., 1913, i, 984) is shown to be 1-ethyl-1-methylcyclohexan-6-one. Like dimethylcyclohexanone (compare this vol., i, 390), it gives a benzyldene derivative, which is 5-benzylidene-1-methyl-1-ethylcyclohexan-6-one, m. p. $78-78.5^\circ$, and a compound, $C_{23}H_{36}O_2$, m. p. $148-150^\circ$. W. G.

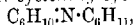
Hydroxycarbonyl Compounds. IV. Synthesis of Aspidinol. P. KARRER and FR. WIDMER (*Helv. Chim. Acta*, 1920, **3**, 392-395. Compare A., 1919, i, 160, 592, 594).—By condensation of butyronitrile with methyl phloroglucinol β -mono-methyl ether in presence of hydrogen chloride, a mixture of two ketones, $OMe \cdot C_6H_4Me(OH)_2 \cdot COPr$, was produced, which can be resolved into its components by fractional crystallisation from light petroleum. The less soluble, m. p. $140-141^\circ$, gave a green colour with ferric chloride, and its identity with aspidinol (Böhm, A., 1902, i, 37) was established by direct comparison. The more soluble, needles, m. p. 116.5° , gave a deep brownish-red colour with ferric chloride, and was called ψ -aspidinol. The two compounds are doubtless the 3- and the 5-butyryl derivatives of the original compound, of which aspidinol has been considered to be the 3-butyryl derivative (Böhm); but this would be contrary to the rule that in such compounds the isomeride with the ketonic group in the para-position to the methoxyl group has a lower melting

point and a greater solubility in light petroleum than the ortho-isomeride (Karrer, A., 1919, i, 592). The distribution of the formulæ between the two compounds is therefore left undecided.

J. K.

The Ketimines: Formation by Catalytic Reduction of Oximes. GEORGES MIGNONAC (*Compt. rend.*, 1920, **170**, 936—938).—

Ketoximes may be reduced in solution in absolute alcohol in the presence of reduced nickel by shaking the solution with hydrogen under atmospheric pressure. The action should be stopped when one molecule of hydrogen has been absorbed for one molecule of oxime. The resulting ketimines undergo hydrolysis by traces of moisture with varying degrees of readiness. In this way, *cyclohexanoneoxime* yielded *N-cyclohexylcyclohexylideneketimine*,

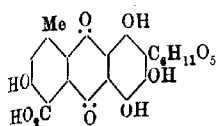


b. p. 117—118°/9 mm., D_D^{20} 0.940, n_D^{20} 1.4972, giving a *hydrochloride*, m. p. 180° (decomp.). *Acetophenoneoxime* yielded *phenylmethyleketimine*, $\text{C}_6\text{H}_5\text{Me}:\text{NH}$, isolated as its *hydrochloride*. *Propiophenoneoxime* gave *phenylethyleketimine*, yielding a *hydrochloride*, m. p. 145°, an *acetyl* derivative, m. p. 126°, and a condensation product, *N- α -phenylpropylphenylethyleketimine*, $\text{C}_6\text{H}_5\text{Et}:\text{N}\cdot\text{CHEtPh}$, b. p. 170—171°/9 mm. *Benzophenoneoxime* yielded *diphenyleketimine*, $\text{C}_6\text{H}_5_2:\text{NH}$, and *phenyl- α -naphthylketoxime* gave *phenyl- α -naphthyleketimine*, $\text{C}_{10}\text{H}_7:\text{C}_6\text{H}_5:\text{NH}$, m. p. 68—69°. The imine group appears to become more stable with respect to water as the groups attached to it become more electronegative in character, the stability of the ketimines described above increasing in the order in which they are given.

W. G.

Carminic Acid. OTTO DIMROTH and HANS KÄMMERER (*Ber.*, 1920, **53**, [B], 471—480).—It has been shown previously (A., 1913, i, 977) that carminic acid is a hydroxyanthraquinone, and the similarity of its absorption spectra and tinctorial properties to those of kermes dye (A., 1916, i, 561) points to the conclusion that it, like the latter, is a hydroxyanthrapurpurin. This is now shown to be the case. It is also found that complete acetylation of carminic acid yields an octa-acetyl derivative. Since, however, only four hydroxyl groups are present in the anthraquinone nucleus, it follows that the remaining four must be present in the side-chain, to which the composition $\text{C}_6\text{H}_{18}\text{O}_5$ has been previously assigned. If, now, one oxygen atom of the latter is present in an ethereal, aldehydic, or ketonic form, a modification of the formula becomes essential, and the side-chain is now considered to be $\text{C}_6\text{H}_{11}\text{O}_5$, the alteration being found to give calculated values which agree with the observed analytical data as well as did those based on the older formula. The constitution of the side-chain has not been fully elucidated. It appears probable that it has a sugar-like structure, although carminic acid is certainly not a glucoside. It contains at least one asymmetric carbon atom, since carminic acid is now found to be optically active, and this phenomenon cannot be attributed to the structure of the nucleus, since kermesic

acid, and also the less closely related laccaic acid, are optically



inactive. The structure of carminic acid, as far as it has been elucidated, is expressed by the annexed formula.

Under suitable conditions, carminic acid is reduced by zinc dust and glacial acetic acid to a leuco-compound, which is converted by atmospheric oxidation into *deoxycarminic acid*, yellowish-red needles, which is best purified by conversion into its *acetyl* derivative, orange-yellow needles, m. p. 245—250° (decomp.). The loss of a β -hydroxyl group during the reduction has its parallel in the cases of kermesic acid and hydroxyanthrapurpurin (Dimroth and Fick, A., 1916, i. 561), whilst the presence of two hydroxyl groups in the 1:4-position relative to one another in the reduction product is shown by its oxidation to a diquinone, from which carminic acid is regenerated by the action of acetic anhydride and sulphuric acid.

Octa-acetylcarmine acid is most conveniently prepared by the action of acetic anhydride and a little concentrated sulphuric acid on carminic acid at the ordinary temperature. When, however, carminic acid is warmed with acetic anhydride in the absence of a catalyst, a *hexa-acetyl* derivative, yellowish-red, cubic crystals, which soften and decompose at 170°, is smoothly formed; two hydroxyl groups in the α -positions on the nucleus remain unaffected, since the substance is readily converted by lead tetra-acetate into an unstable diquinone, which is reduced by sulphurous acid to the parent substance.

Carminic acid has $[\alpha]_{405}^{25} + 51.6^\circ$ in aqueous solution, whilst octa-acetylcarmine acid has $[\alpha]_{415}^{25} + 80.55^\circ$ in chloroform. Deoxycarmine acid is strongly active, but the acetyl derivatives of kermesic and laccaic acids are completely inactive. H. W.

The Acetylation of Hydroxyanthraquinones and Anthra-diquinones. OTTO DIMROTH, OTTO FRIEDEMANN, and HANS KÄMMERER (*Ber.*, 1920, 53, [B], 481—487).—In connexion with the observations made during the acetylation of carminic acid (preceding abstract), the authors have investigated the behaviour of various hydroxyanthraquinones when similarly treated, and find that, quite generally, the hydroxyl groups in the α -position are far less readily attacked than those in the β -position. A convenient method for the preparation of β -acetylated derivatives consists in allowing calculated quantities of acetic anhydride and the hydroxy-compound to react in cold pyridine solution; with an excess of anhydride, the α -hydroxy-groups are also attacked.

2-Hydroxyanthraquinone is completely acetylated when boiled for ten minutes with acetic anhydride, whilst, under similar conditions, 1-hydroxyanthraquinone is scarcely attacked; after six hours' treatment, however, the latter is largely acetylated. *Purpurin 2-acetate*, prepared from the components in hot pyridine solution, forms orange-coloured crystals, m. p. 172—173°, and is oxidised by lead peroxide or lead tetra-acetate to *2-acetyl-purpurin*.

quinone, straw-yellow, slender needles, m. p. 167—168°. *Alizarin bordeaux 2-acetate*, $C_6H_2(OH)_2$ $\begin{matrix} \text{CO} \cdot \text{C} \cdot \text{C}(\text{OH}) : \text{C} \cdot \text{OAc} \\ \text{CO} \cdot \text{C} \cdot \text{C}(\text{OH}) : \text{CH} \end{matrix}$, forms red needles, m. p. 246—247°. *Hydroxyanthrapurpurin 2:7-diacetate* crystallises in orange-coloured needles, m. p. 224—225°, and is oxidised by lead tetra-acetate to an unstable diquinone, which was not obtained in the crystalline condition.

An improved process for the oxidation of quinzarin to 1:4:9:10-anthradiquinone, either by means of lead peroxide or lead tetra-acetate, has been worked out (compare Dimroth and Schultze, A., 1916, i, 563). In a similar manner, mono- and dibromoquinizarin are oxidised to 3-bromo-1:4:9:10-anthradiquinone, straw-yellow, flat needles, m. p. 212—214° (decomp.), and 2:3-dibromo-1:4:9:10-anthradiquinone, yellowish-green, six-sided leaflets, which become red without melting at 300°, respectively.

Purpurinquinone 2-acetate is transformed by acetic anhydride and sulphuric acid into tetra-acetoxyanthraquinone, m. p. 205°, which is hydrolysed to 1:2:3:4-tetrahydroxyanthraquinone.

H. W.

Constituents of Indian Turpentine from *Pinus longifolia*, Roxb. I. JOHN LIONEL SIMONSEN (T., 1920, 117, 570—578).

Hot Vulcanisation of Caoutchouc. F. KIRCHHOFF (*Kolloid Zeitsch.*, 1920, 26, 168—173).—A theoretical paper in which the author criticises the views of Harries (*Untersuch. natürlich. Künstlich. Kautschukarten*) (A., 1916, i, 659). The author claims that, previously to Harries, he had put forward the physico-chemical principles on which the hot vulcanisation of rubber takes place. Several experiments with lead oxide and lead sulphide mixed with small quantities of sulphur and a small quantity of sulphur-free organic catalyst are described, which show that vulcanisation can be effected with other substances than sulphur. In view of the advances in the knowledge of the constitution of rubber by the work of Harries, and the behaviour of depolymerised rubber on bromination (Schmitz, *Gummi Zeit.*, 1919, 34, 1937), it is held that the chemical interpretation of the vulcanisation process is likely to undergo many modifications.

J. F. S.

Artemisin. P. BRUTOLO (*Gazzetta*, 1920, 50, i, 109—113).—The conclusions concerning the constitution of artemisin drawn from the author's previous investigations (A., 1904, i, 177; 1905, i, 224, 897; 1908, i, 560; 1911, i, 898) are briefly summarised. Short descriptions are now given of the products obtained by the action of various reagents on artemisin; the constitutions of these products are to be discussed later.

The action of dilute sulphuric acid (1:1) on artemisin at temperatures below 60° yields a white, crystalline compound, m. p. 236°, $[\alpha]_D -84.16^\circ$, insoluble in alkali carbonate solution, but soluble in alkali hydroxide solution, from which it is precipitated unaltered by means of carbon dioxide; in this compound, the

lactonic linking is preserved, but not the ketonic carbonyl, which appears to be converted into the phenolic group, C·OH, with formation of a desmotropo-artemisin. The action of more concentrated sulphuric acid at 100° gives a red oil, which solidifies on cooling and dissolves almost completely in alkali carbonate solutions, and appears to be identical with the dextrorotatory artemisic acid obtained by the action of hydrochloric acid on artemisin.

Treatment of artemisin with hydriodic acid and red phosphorus yields an acid compound, which somewhat resembles artemisic acid, but has the lower m. p. 98° and the higher specific rotation $[\alpha]_D +72.3^\circ$. This compound forms white crystals, but gradually reddens and partly resinifies on exposure to light. It is also formed when artemisin is treated with iodine in alcoholic solution, and is probably a product of the further reduction of artemisic acid, from which it is apparently formed by reduction with sodium amalgam.

Acetic anhydride does not act on artemisin, but acetyl chloride converts it into the pale yellow *acetyl* compound, $C_{15}H_{17}O_4Ac$, m. p. 200°, $[\alpha]_D -52.60^\circ$, which, when hydrolysed with potassium hydroxide, gives, not artemisin, but a moderately stable acid compound, m. p. 200°.

According to the conditions employed, the action of chlorine on artemisin yields one of three chloro-derivatives, m. p. 135°, 230°, and 180° respectively.

Reduction of artemisin by means of sodium amalgam gives, in almost theoretical yield, a crystalline, optically inactive, acid compound, m. p. 170°, the barium salt and *ethyl* ester of which have been analysed.

Exposure to light of a solution of artemisin in 50% acetic acid or about two months at a temperature never exceeding 35° results in the formation mainly of a white, crystalline compound, m. p. 142°, which exhibits lactonic and phenolic functions, and appears to be a new desmotropic form of artemisin. Exposure of the same solution to light during the summer months, when the temperature may sometimes reach 45°, yields principally a white acid, m. p. 168°.

Barium hydroxide on heating strongly attacks artemisin, giving ill-defined decomposition products; from the resinous substances obtained, an acid compound, m. p. 168°, which does not react with phenylhydrazine, was with difficulty isolated in an impure condition.

T. H. P.

Action of Sulphuric Acid on Artemisin: desmotropo-Artemisin. P. BERTOLO (*Gazzetta*, 1920, 50, i, 114—119. Compare preceding abstract).—l-desmotropo-Artemisin, $C_{15}H_{18}O_4$, prepared by the action of dilute sulphuric acid on artemisin at temperatures below 60°, forms white, flattened crystals, m. p. 236°, and, when treated with boiling solutions of alkali or alkaline-earth hydroxides, yields the corresponding salts of an unstable, monobasic hydroxy-acid; when the latter is liberated, it undergoes ready conversion into the original lactone. With sulphuric

acid and ferric chloride, *l*-desmotropo-artemisin gives neither the santonin nor the artemisin reaction, but remains undissolved and without coloration even in the hot.

In aqueous solution, the barium salt, $(C_{14}H_{19}O_3 \cdot CO_2)_2Ba$, gives: with silver nitrate, the flocculent silver salt, which turns brown in the light and decomposes with formation of a silver mirror in the hot; with copper sulphate, a bluish-white precipitate; with lead acetate, a flocculent, white precipitate, somewhat soluble in excess of the reagent; with ferric chloride in the cold, no precipitate, whereas in the hot, a red, flocculent precipitate slowly forms.

Acetyl-l-desmotropo-artemisin, $C_{15}H_{17}O_8 \cdot OAc$, forms aggregates of radiating, shining crystals, m. p. 154–155°, $[\alpha]_D - 66.90^\circ$.

Zinc dust and acetic acid are without action on *l*-desmotropo-artemisin, no acid analogous to the santonous acids being obtained in this way.

T. H. P.

Rutin, the Flavone Pigment of *Escholtzia californica*, Cham.
CHARLES E. SANDO and H. H. BARTLETT (*J. Biol. Chem.*, 1920, 41, 495–501).—Nearly 5% of rutin is present in the petals of *Escholtzia californica*. It crystallises in fine, dense tufts of silky crystals, m. p. 190–192° (uncorr.). The accepted constitution of rutin (quercetin-glucosyl-rhamnoside) is supported. Quercetin, m. p. 310°, glucosazone, and rhamnosazone were isolated after acid hydrolysis.

J. C. D.

Solubilities of Theobromine. RAYMOND V. WADSWORTH (*Analyst*, 1920, 45, 133–134).—The recorded solubilities for theobromine are inaccurate, the error apparently originating with Mitscherlich, whose values for the solubility of the alkaloid in chloroform, ether, and water are much too high. The impurity to which this is to be attributed appears to have been caffeine. The following amounts of pure theobromine were dissolved by different solvents at 15.5° and at their boiling points respectively: ethylether, 0.003 and 0.003; benzene, 0.005 and 0.010; carbon tetrachloride, 0.020 and 0.040; chloroform, 0.060 and 0.070; boiling absolute alcohol, 0.100; water, 0.060 and 0.700; tetrachloroethane, 0.090 and 0.870; and aniline, 0.650 and 8.000%.

C. A. M.

The Tropine and Cocaine Series. II. JULIUS VON BRAUN and KURT RATH (*Ber.*, 1920, 53, [B], 601–614).—In continuation of previous work (von Braun and Müller, A., 1918, i, 233), the authors have further examined the influence of the relative positions of the hydroxyl group and the basic nitrogen atom and of the introduction of double bonds on the physiological activity of the tropeines. Sufficient evidence has not, however, been collected to enable any general conclusion to be drawn with regard to mydriatic action. The anæsthetic power, however, seems to attain its maximum when the hydroxyl group is in the γ -position to the nitrogen atom, and, if this condition is fulfilled, to be independent of any

N- β -Hydroxyethylnortropidine (annexed formula), colourless, rather viscous oil, b. p. 115–117°; 12 mm.; is prepared by the action of ethylene oxide on nortropidine in chloroform solution in the presence of a trace of water; it gives a *platinichloride*, long, yellow needles, m. p. 158°, a *picrate*, orange leaflets, m. p. 162°, and a coarsely crystalline *methiodide*, which does not melt below 270°. The *benzoyl* derivative is an oil, the *hydrochloride* of which has m. p. 184°. The *tropyl* derivative closely resembles that obtained from ϵ -hydroxyamylnortropane; the oily *methiodide* could, however, be converted into a crystalline *platinichloride*, $C_{28}H_{30}O_6N_2Cl_6Pt$, yellow, crystalline powder, m. p. 139° (decomp.), after darkening above 120°.

The *benzoyl* derivative of *N*- γ -hydroxypropylnortropidine, prepared from nortropidine and γ -bromopropyl benzoate, is a moderately viscous, non-crystallisable oil, which yields a *hydrochloride*, m. p. 165–167°. It appears to be smoothly hydrolysed to *N*- γ -hydroxypropylnortropidine, but lack of material prevented the fuller investigation. H. W.

Triphenylpyridine, Acetophenone, and Acetophenine. W. DILTHEY and F. KIEFER (*Ber.*, 1920, 53, [B], 621–622).—It has been shown recently by Reddelien (this vol., i, 316) that Engler's acetophenone [described in the latest edition of Beilstein's *Handbuch* as acetophenine] is identical with triphenylpyridine. This is confirmed by the authors, who have further prepared the trinitrotriphenylpyridine described by Engler and Heine. Like Reddelien, they find that the yields of triphenylpyridine obtainable from acetophenone and benzaldehyde or benzonitrile are very small, and consider the substance to be most conveniently prepared by the action of ammonia on arylated pyrilium salts. H. W.

Formation of 4-Benzyl-3-methyl-5-pyrazolone. FRANCESCO CHERCHI (*Gazzetta*, 1920, 50, i, 120–127).—4-Benzyl-3-methyl-5-pyrazolone, $CO < \begin{matrix} NH \\ | \\ CH(CH_2Ph) \cdot CMe \end{matrix} N$, obtained by the action of hydrazine hydrate on methyl or ethyl α -benzylacetoacetate in aqueous-alcoholic solution, forms white needles, m. p. 228–229°. When treated in alcoholic solution with sodium ethoxide, it yields the sodium salt, $C_{11}H_{11}ON_2Na$, and a compound, which crystallises in needles, m. p. 141–142°. The *picrate*, $C_{11}H_{12}ON_2 \cdot C_6H_3O_2N_3$, forms yellow needles, m. p. 154.5°. 1(?)-Acetyl-4-benzyl-3-methyl-5-pyrazolone, $C_{11}H_{11}ON_2Ac$, forms silky, white needles, m. p. 128–129°.

4-Benzyl-3-methyl-1(?)-ethyl-5-pyrazolone, $C_{11}H_{11}ON_2Et$, prepared by the action of ethyl iodide on the pyrazolone dissolved in sodium ethoxide solution, crystallises in large, colourless prisms,

m. p. 177°, and is accompanied by a yellow, oily compound, which is to be investigated later.

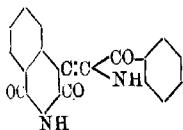
T. H. P.

Dibutylbarbituric Acid. O. KAMM and E. H. VOLLWEILER (U.S. Pat. 1331712).—To the solution of 40 grams of sodium in 1000 c.c. of absolute alcohol are added 157 grams of ethyl dibutylmalonate (prepared by the interaction of butyl bromide and ethyl malonate in the presence of 2 mols. of sodium ethoxide) and 50 grams of carbamide, and the mixture is heated for six hours under pressure at 100–110°. The alcohol is then removed by distillation, water is added, and dibutylbarbituric acid, colourless needles, m. p. 158°, is precipitated by hydrochloric acid, the yield being 130 grams. The substance has pronounced sedative properties with but slight toxicity.

CHEMICAL ABSTRACTS.

The Cyanine Dyes. I. The Constitution of the *iso*Cyanines. WILLIAM HOBSON MILLS and ROBERT SCOTT WISHART (T., 1920, 117, 579–587).

Dyes Derived from 1:3-Dioxy*iso*quinoline [*o*-Homophthalimide]. W. HERZOG (*Ber.*, 1920, 53, [B], 564–567).—Homophthalimide is readily condensed with α -isatinanilide in acetic anhydride solution to yield 1:3-dioxy-4-*iso*quinoline-2'-*indoleindigo*



[1:3-diketo-4(2')-indoxyltetrahydro*iso*quinoline] (annexed formula), reddish-violet, amorphous powder, m. p. about 270°, which is readily decomposed by dilute solutions of alkali hydroxides, but can be converted into its leuco-compound by zinc dust and acetic acid; it gives dark violet shades on wool. Similarly,

β -isatinanilide yields 1:3-dioxy-4-*iso*quinoline-3'-*indoleindigo* [1:3-diketo-4(3')-indoxyltetrahydro*iso*quinoline], brown needles, m. p. about 300°, which is slowly decomposed by cold alkali hydroxide solutions. It can be reduced by hyposulphite in the presence of alkali or by zinc and acetic acid, but the vat is devoid of tinctorial properties. 1:3-Dioxy-4-*iso*quinoline-2'-thionaphthenindigo [1:3:3'-Tri-keto-4(2')-thionaphthentetrahydro*iso*quinoline], from *o*-homophthalimide and thionaphthenquinoneanilide, crystallises in yellowish-red needles, m. p. about 250° (decomp.). The leuco-compound can be prepared in the usual manner, but has little affinity for the fibres, giving fugitive cherry-red shades on wool and pale pink tones on cotton.

H. W.

The Stabilisation of Nitrous Acid in Connexion with Reactions carried out with this Compound; Applications to Diazotisation. E. BRINER and R. JONAS (*Helv. Chim. Acta*, 1920, 3, 366–369).—The reversibility of the decomposition of nitrous acid into nitric acid, nitric oxide, and water suggests that solutions of the acid should be stable in presence of nitric oxide under pressure. This principle has been successfully applied to

the diazotisation of dinitroaniline, tribromoaniline, and *p*-sulpho-benzeneazo- α -naphthylamine, which is difficult under ordinary conditions, by condensing nitrogen trioxide in a cooled tube containing the amino-compound and hydrochloric acid, sealing the tube, and allowing the temperature to rise. Picramide was not diazotised by this treatment. The value of the use of compressed air, proposed in the case of the last of the above three compounds (D.R.-P. 143450), is probably to be explained in the same way.

J. K.

Origin of the Humin formed by the Acid Hydrolysis of Proteins. V. ROSS AIKEN GORTNER and GEORGE E. HOLM (*J. Amer. Chem. Soc.*, 1920, **42**, 821—827. Compare this vol., i, 400).—Pursuing their inquiry as to the nature of the reaction by which humin is produced, the authors prepared artificial mixtures of thirteen of the amino-acids commonly obtained by the hydrolysis of proteins. Such mixtures, when boiled for twenty-four hours with hydrochloric acid in presence of either trioxymethylene or tyrosine and trioxymethylene, or tryptophan and tyrosine, gave no insoluble humin; but this was produced when tryptophan, tyrosine, and formaldehyde were present. The reaction is therefore dependent on the presence of tryptophan, and can serve as a quantitative measure of the amount of this substance present. Similarly, soluble humin is derived from tyrosine, but, owing to its solubility, the amount is not a quantitative measure of the tyrosine. Phosphotungstic humin was produced to an equal extent in all the experiments, and may represent only an adsorption phenomenon. It is specially noted that the amino-group of cystine was not displaced in these experiments.

J. K.

The Action of Thrombin on Fibrinogen. JOHN OGLETHORPE and WAKELIN BARRATT (*Biochem. J.*, 1920, **14**, 189—209).—Fibrinogen in solution is diphasic, consisting of a concentrated phase which is dispersed, and a dilute phase which is continuous.

The action of thrombin is to form fibrin only from the fibrinogen in the concentrated phase, and is purely catalytic. A hypothesis of the mode of formation of fibrin fibrils is advanced. When fibrinogen in the concentrated phase is converted into fibrin, the equilibrium between the phases is disturbed, and more fibrinogen passes from the continuous to the disperse phase. This is then converted into fibrin. The "growth" of fibrin fibrils proceeds at a unimolecular rate.

J. C. D.

The Mode of Union of Iron in the Prosthetic Group of Blood Pigments and the Constitution of Hæmin. WILLIAM KÜSTER (*Ber.*, 1920, **53**, [B], 623—633).—The communication is mainly devoted to a reasoned, adverse criticism of the views propounded by Willstätter (*A.*, 1915, i, 289). The author maintains his ideas (*A.*, 1912, i, 670) that two of the nitrogen atoms in hæmin are basic, and are so related to the two carboxyl groups that one nitrogen is united to one carboxyl group as

a betaine complex, leaving one carboxyl group, which alone can be easily esterified. In support of this hypothesis, it is now shown that the *diethyl ether* of *haematoporphyrin*, red, crystalline powder without a distinct melting point (the *silver* salt and the very hygroscopic *dihydrochloride* are described), is transformed by a boiling 1% solution of hydrogen chloride in ethyl alcohol into an isomeric *diethyl ether*, needles (and is thus not esterified), which is slowly converted by *N*-hydrochloric acid into the dihydrochloride of the original material; with more concentrated alcoholic hydrochloric acid solution, *haematoporphyrin diethyl ether* is converted into *tetraethylhaematoporphyrin*, steel-blue powder, m. p. about 91–93°. The action of diazomethane on *haemin* has been investigated previously (A., 1918, i, 199), and this is now shown to differ fundamentally from its effect on the hydrochlorides of the triphenylmethane dyes, since, in the former class, the halogen atom is never removed, whilst in the latter series it is eliminated as methyl chloride, and the leucobase is formed. It is therefore probable that the halogen atom is directly united to the iron atom, and this is rendered more probable, since measurement of the electrolytic conductivity of *haemin* and its dimethyl ester in pyridine solution shows them to behave in the same manner as inorganic salts.

H. W.

Refractivity of Hæmoglobin in Solution. FREDERICK H. HOWARD (*J. Biol. Chem.*, 1920, **41**, 537–547).—The refractive index of hæmoglobin solutions varies directly with concentration and is independent of the presence of other proteins, and of bases and salts in low concentration. The value of α for hæmoglobin is 0.00183.

J. C. D.

Hæmocyanin. III. CH. DHÉRÉ (*J. Physiol. Path. gén.*, 1919, **18**, 503–526; from *Physiol. Abstr.*, 1920, **5**, 7).—Hæmocyanin of the snail can be obtained in a crystalline form by dialysis against distilled water, by exposing the blood to a potential difference of 120 volts after dialysis, or cooling the supernatant liquid in the dialyser in ice. It may be purified by solution in a very small amount of *N*/500-sodium sulphate, from which it crystallises on cooling in ice. Hæmocyanin of the rock lobster can be crystallised by the last method, and that of cephalopods by the method of Hopkins and Pinkus, using concentrated ammonium sulphate. The varying forms of crystals obtained are probably due to differences in the proportions of water of imbibition, not of hydration.

W. G.

Properties of the Nucleotides obtained from Yeast Nucleic Acid. P. A. LEVENE (*J. Biol. Chem.*, 1920, **41**, 483–493).—The work reported in this paper was carried out in order to clear up the discrepancies in the reported properties of the nucleotides from yeast.

Adenosinephosphoric acid, $C_{10}H_{14}O_7N_5P_6H_2O$, is the most insoluble of the four nucleotides. It decomposes with effervescence at 195°

(corr.); $[\alpha]_D^{20} - 40.5^\circ$ in 1% aqueous solution, -40.5° to -44.5° in 5% aqueous-ammonia solution; $[\alpha]_D^{20} - 38.0^\circ$ in 10% hydrochloric acid, -59.5° in 2% sodium hydroxide, -66.0° in 5% sodium hydroxide.

Guanosinephosphoric acid, $C_{10}H_{14}O_8N_5P_2 \cdot 2H_2O$, contracts on heating at 175° (corr.) and decomposes at 180° . $[\alpha]_D^{20} - 7.5^\circ$ in water, $+1.5^\circ$ in 10% hydrochloric acid; $[\alpha]_D^{20} - 44.0^\circ$ in 5% aqueous ammonia; $[\alpha]_D^{20} - 57.0^\circ$ in 2% aqueous sodium hydroxide, -65.0° in 5% aqueous sodium hydroxide.

Cytidinephosphoric acid, $C_9H_{14}O_8N_3P_2$, prisms, decomp. $230-233^\circ$ (corr.), slow heating. $[\alpha]_D^{20} + 40.0^\circ$ to $+48.5^\circ$ in water; $[\alpha]_D^{20} + 26.0^\circ$ in 10% hydrochloric acid, $+44.5^\circ$ in 5% ammonia, $+25.5^\circ$ in 2% sodium hydroxide; $[\alpha]_D^{20} + 1.0^\circ$ and -21.0° , respectively, in 5 and 10% sodium hydroxide.

Uridinephosphoric acid, $C_9H_{13}O_8N_2P_2$, small bunches of needles, m. p. 198.5° (corr.; decomp.). $[\alpha]_D^{20} + 9.5^\circ$ in water, $+6.5^\circ$ in 2% sodium hydroxide, and -15.0° in 5% sodium hydroxide.

Monoammonium salt of uridinephosphoric acid, fine, curved, felted needles, decomp. 240° . $[\alpha]_D^{20} + 10.5^\circ$ in water; $[\alpha]_D^{20} + 2.5^\circ$ in 10% hydrochloric acid, $+14.0^\circ$ in 5% ammonia; $[\alpha]_D^{20} + 1.5^\circ$, -16.0° , -26.0° , respectively, in 2, 5, and 10% sodium hydroxide.

Adenosine has $[\alpha]_D^{20} - 60.0^\circ$ in aqueous solution, -43.5° in 10% hydrochloric acid, -68.5° in 5% sodium hydroxide.

Uridine, $[\alpha]_D^{20} + 4.0^\circ$ in water, $+5.0^\circ$ in 10% hydrochloric acid, -6.0° in 5% sodium hydroxide.

The changes in the optical rotation are probably due to several causes, amongst which tautomeric changes possibly play an important part. Adenosine and uridine show the same character of optical rotation as the corresponding nucleotides. J. C. D.

The Theory of Gels. II. The Crystallisation of Gelatin.

SAMUEL CLEMENT BRADFORD (*Biochem. J.*, 1920, **14**, 91-93).—It has been previously shown (A., 1919, ii, 139) that the reversible gelation of the natural emulsoids is a crystallisation process resulting from the viscosity of these substances and from their very small diffusion constants, which greatly retard the crystallisation of the cooling sols, altering the accumulation of a large excess concentration. Hydrosols of "crystal" leaf gelatin of 0.5 and 0.3% were made, quickly heated to 100° , and filtered into thoroughly clean, covered crystallising dishes. A small amount of mercuric chloride was added to prevent bacterial growth, and the solutions were allowed to evaporate at the ordinary temperature. By this means a precipitate, consisting of microscopic spherules 0.25μ to 0.28μ in diameter, was obtained. From these results, it cannot be doubted that gelatin crystallises from water exactly as indicated by von Weimarn's theory. J. C. D.

Swelling of Gelatin in Hydrochloric Acid and Sodium Hydroxide. DOROTHY JORDAN LLOYD (*Biochem. J.*, 1920, **14**, 147-170).—This paper furnishes further experimental support to

the theory which holds that gelatin is an amphoteric colloid, the neutral form of which is stable only at the isoelectric point (P_H 4.6, 20°). The molecular weight is 10,000 or some multiple of 10,000. This neutral gelatin is only slightly soluble in hot water, and is insoluble in cold water. It may, however, combine with water to form complexes, perhaps of the nature of hydrates or solid solutions. On the acid side of P_H 4.6, gelatin functions as a multi-acid base, giving rise to ionisable hydrochlorides, and at P_H 2.5 practically all the protein exists in the form of such salt. At lower hydrogen-ion concentrations than that of the isoelectric point, gelatin acts as a polybasic acid, forming ionisable gelatinates with bases such as sodium. The reaction with hydrochloric acid is reversible, that with sodium hydroxide irreversible. The formation of keto-salts in acids and enol salts in alkalis is postulated.

Regarding gels, the author is of the opinion that they are two-phase structures consisting of a solid framework of precipitated neutral gelatin, with which is combined a certain amount of water, and an interstitial fluid which is a solution of gelatin salt. The volume of any system in the gel condition is determined by two opposing sets of forces, the elastic forces of the solid framework, which tend to make the volume contract, and the osmotic forces of the ionised gelatin salts dissolved in the interstitial fluid, which tend to make the volume expand. Hence neutral gelatin, being only one phase, cannot make a stable gel, but will make a gel which will be free to contract. Similarly, since the salt form of gelatin is a single phase, such cannot form a gel. Gelatin in this form will only form sols with water.

The volume occupied by a gelatin gel swelling in a fluid medium depends on the ratio of the mass of the dissolved electrolyte to the mass of gelatin, on the geometrical form of the gel, and also on the hydrogen-ion concentration of the medium. Gels which are swelling in a weakly acid or alkaline medium lose water on being transferred to an atmosphere of saturated vapour. The amount of water lost is a function of the reaction of the previous external fluid. This loss follows from the elastic properties of the gel, and is shown to be in accordance with the membrane theory of Donnan. Van Bemmelen's theory that the surface of a gel is to be regarded as a solid membrane perforated by pores is confirmed by observation.

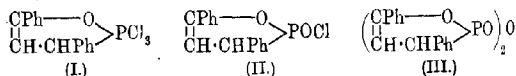
J. C. D.

Chemical Kinetics of Catalase. I. Catalase from Phyl. mit., Riv. EIICHI YAMASAKI (*Sci. Rep. Tôhoku Imp. Univ.*, 1920, 9, 13—58. Compare this vol., i, 194).—The velocity of decomposition of hydrogen peroxide by means of the catalase from *Phyllostachys mitis*, Riv., has been investigated at 0° , 10° , 12.5° , 18° , and 25° . The catalase is obtained by crushing an edible sprout from a species of bamboo with water saturated with toluene. It was observed that the activity of the catalase steadily decreased during the reaction. The velocity of the reaction is represented by the equations $-dC/dt = kEC$ and $-dE/dt = -k'/k \cdot dC/dt = k'EC$, where E and C are the concentration of the enzyme and

hydrogen peroxide respectively, and k and k' the reaction constants. The decrease of activity of the catalase is caused by the substrate and the product of the reaction, and its rate is approximately proportional to the principal reaction. The decrease of activity cannot be attributed to the change of the concentration of hydrogen ions produced by the decomposition of hydrogen peroxide, because a similar decrease of activity also occurs in acid solutions where the hydrogen-ion concentration is constant. The relative activity of the enzyme is always proportional to its concentration if the concentration of the hydrogen ion is maintained throughout the experiment. In a very dilute solution of hydrogen peroxide and a relatively concentrated solution of the enzyme, the activity increases in the first stage and then decreases. This may probably be explained by the following: (i) The ordinary reaction would be carried out at a rate somewhat higher than that calculated for a first-order reaction. (ii) The rate is decreased by oxygen and hydrogen peroxide in ordinary cases. (iii) Such effects are observed only in the course of reactions in very dilute solutions, because the concentrations of both the substrate and the product are very small, that is, the velocity constant has a maximum value. (iv) The retardation occurs with a measurable velocity, which is approximately proportional to the principal reaction. This explanation is in keeping with the observations of Waentig and Steche (A., 1913, i, 304) for solutions which were rapidly stirred in a vacuum.

J. F. S.

A New Type of Addition Reaction. JAMES B. CONANT and ALAN A. COOK (*J. Amer. Chem. Soc.*, 1920, **42**, 830—840. Compare A., 1918, i, 74).—The formation of ketophosphinic acids by the interaction of $\alpha\beta$ -unsaturated ketones and phosphorus trichloride in presence of acetic acid is complete before the addition of water to the mixture, since the acid may be precipitated by the addition of benzene; acetyl chloride is the other product of the reaction. The first stage in the reaction with phenyl styryl ketone probably consists in the formation of the compound (I), since if acetic anhydride be used at the ordinary temperature in place of acetic acid, a mixture is produced of the acid chloride (II), a light-coloured, viscid oil, with an amount of the anhydride (III) which increases with the quantity of acetic anhydride employed. Water readily converts these compounds into β -benzoyl- α -phenylethyl-



phosphinic acid, and they combine with bromine to give products from which, by decomposition with water, β -bromo- β -benzoyl- α -phenylethylphosphinic acid, $\text{CPh} \cdot \text{CHBr} \cdot \text{CHPh} \cdot \text{PO}(\text{OH})_2$, m. p. 196° , is produced. This compound may also be prepared by bromination of β -benzoyl- α -phenylethylphosphinic acid. It is at once converted by sodium hydrogen carbonate, sodium carbonate or sodium hydroxide into phenyl styryl ketone, sodium bromide

and sodium phosphate. Its *monophenyl* ester, m. p. 179°, was produced by the action of phenol on the crude chloride obtained by treating with thionyl chloride either the acid or the product of the condensation of phenyl α -bromostyryl ketone with phosphorus trichloride and acetic acid; it is best prepared by brominating phenyl β -benzoyl- α -phenylethylphosphinate, m. p. 146°, which is obtained from the corresponding acid through the chloride. Diphenyl β -benzoyl- α -phenylethylphosphinate, m. p. 125°, results in small quantities in the preparation of the monophenyl ester, but is best obtained by treating the acid with two molecular proportions of thionyl chloride, and subsequently with phenol. It dissolves in cold sodium ethoxide solution, and is converted into the monophenyl ester. The monophenyl ester is also obtained by treating the mixture of the compounds (II) and (III) with phenol. It is accom-

panied by the compound, $\begin{array}{c} \text{CPh} \text{---} \text{O} \\ | \\ \text{CH} \cdot \text{CHPh} \end{array} > \text{PO} \cdot \text{OPh}$, an oil insoluble in

cold aqueous alkali, but convertible into the monophenyl ester either by solution in alcoholic sodium hydroxide solution or by treatment first with hydrogen chloride at 125° and then with water.

J. K.

Improved Method for the Preparation of Primary Arsanilic Acid.

HAROLD C. CHEETHAM and JOHN H. SCHMIDT (*J. Amer. Chem. Soc.*, 1920, **42**, 828—829).—Fichter and Elkind's process for the preparation of arsanilic acid (A., 1916, i, 444) gives only a fair yield, but better than that of Kober (A., 1919, i, 182). It was found best to heat a mixture of dry arsenic acid ($\frac{1}{4}$ gram-mol.) with aniline ($\frac{1}{3}$ gram-mol.) for twelve hours at 150—160°, the yield of purified product being 26%. J. K.

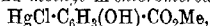
Aromatic Mercuridicarboxylic Esters.

WALTER SCHOELLER, WALTER SCHRAUTH, and RICHARD HUETER (*Ber.*, 1920, **53**, [B], 634—643).—The non-toxicity of mercuridipropionic acid and mercuridibenzoic acid in comparison with the highly toxic mercury diaryls or dialkyls has been shown by Müller, Schrauth, and Schoeller (A., 1911, ii, 755) to be attributable to the excretion of the former unchanged from the organism in which the latter are decomposed. The present investigation deals with the production of mercuridicarboxylic acids, which would be more readily decomposed, and of their derivatives, which would not be eliminated, the ultimate object being an examination of their toxicity, the results of which are described elsewhere.

Methyl o-chloromercuribenzoate. $\text{HgCl} \cdot \text{C}_6\text{H}_4 \cdot \text{CO} \cdot \text{Me}$, needles, m. p. 162° after softening at 142°, is prepared by heating methyl benzoate, mercury acetate, and glacial acetic acid, separation of the methyl di- and mono-*o*-acetoxymercuribenzoates by means of acetone, and treatment of a solution of the latter in aqueous alcohol with sodium chloride solution. It is converted by hydrogen

sulphide in methyl-alcoholic solution into *methyl sulphidodimercuri-o-benzoate*, $S(Hg \cdot C_6H_4 \cdot CO_2Me)_2$, white, amorphous powder, which softens and gradually darkens when heated; the latter is transformed at 120° into *methyl mercuridi-o-benzoate*, colourless crystals, which is hydrolysed by *N*-sodium hydroxide solution to mercuridi-benzoic acid, identical with the product prepared by Pesci in another manner.

Methyl acetoxymercurisalicylate, m. p. 202° (corr.) after slight previous softening, and *methyl m-chloromercurisalicylate*,



are prepared in the same manner as the corresponding benzoates, and are similarly transformed into *methyl sulphidodimercurisalicylate*, white, amorphous powder, and *methyl mercuridisalicylate*, m. p. $178-180^\circ$ (corr.). *Ethyl acetoxymercurisalicylate*, needles, grouped in clusters, m. p. 206° (corr.) after softening at 200° , is converted by saturated aqueous sodium thiosulphate solution into *ethyl mercuridisalicylate*, m. p. 193° (corr.).

Methyl mercuridanthranilate forms small, yellow needles, m. p. $196-197^\circ$ (corr.) after slight previous decoloration, whilst *methyl mercuridi-p-aminobenzoate* crystallises in yellow needles, m. p. 176° (corr.).

H. W.

Phenylthiolmercuri-chloride. H. LECHER (*Ber.*, 1920, 53, [B]. 568-577).—In continuation of previous investigations (A., 1916, i. 41), the author has endeavoured to prepare a mixed mercantide of the type $R'S \cdot Hg \cdot SR''$, and, for this purpose, has studied the action of phenylthiolmercuri-chloride, $HgCl \cdot SPh$, on sodium ethyl sulphide: reaction is found to proceed, for the greater part at any rate, in accordance with the equation $2HgCl \cdot SPh + 2NaSEt = 2NaCl + Hg(SPh)_2 + Hg(SEt)_2$, although the complete absence of the mixed mercantide is not definitely proved. The possibility that the chloride should be formulated $Hg(SPh)_2 \cdot HgCl$, appeared to be discounted by determinations of the molecular weight in boiling ethyl acetate solution, which indicated the simple structure. The explanation of the course of the reaction is found in the observation that phenylthiolmercuri-chloride is dissociated in solution into mercury phenylmercaptide and mercuri-chloride, $2HgCl \cdot SPh \rightleftharpoons Hg(SPh)_2 + HgCl$. The chloride can be readily prepared by mixing solutions of equivalent amounts of mercury phenylmercaptide and mercuric chloride, and the latter can also be extracted from solutions of the mercuri-chloride in organic solvents by sodium chloride solution. Further, if a solution of phenylthiolmercuri-chloride in pyridine is treated with ammonia, mercuric chloride is precipitated, whilst mercury phenylmercaptide remains in solution.

Mercury phenylmercaptide has been shown to undergo partial dissociation when heated into phenyl disulphide and mercury (*loc. cit.*). It is now shown that phenylthiolmercuri-chloride behaves in an analogous manner; when heated, it exhibits thermochromism, and melts at 191.5° , dissociating for the greater part

into diphenyl disulphide and mercurous chloride. A small portion, however, always remains on decomposition, and, conversely, small amounts of phenylthiolmercuri-chloride can be obtained by heating a mixture of the disulphide and mercurous chloride. H. W.

Physiological Chemistry.

Variations in the Chemical Composition of Human Blood.

FREDERICK S. HAMMETT (*J. Biol. Chem.*, 1920, **41**, 599—615).—Whilst the total nitrogen, non-protein nitrogen, and sugar of the blood vary in the same person from week to week, there is a tendency for the level of these variations to be characteristically individual. There is no practical difference between the absolute amounts of the constituents in bloods taken fourteen hours after food and three and a-half hours after breakfast. The absolute amount of creatinine is constant for the individual and for the species. The variations of urea, uric acid, creatine, and other non-protein nitrogenous substances are discussed. J. C. D.

Anti-coagulating and Hæmolyzing Action of Sodium Nucleate. Action on Brewer's Yeast. DOTON (*Compt. rend.*, 1920, **170**, 966—967).—Sodium nucleate used in the form of a powder possesses an anti-coagulating power and exerts a very energetic hæmolyzing action. It also prevents the decomposition of sugar into alcohol and carbon dioxide by brewer's yeast.

W. G.

Effect of Alkali Fluorides on Digestion. GROSSERON (*Ann. Chim. anal.*, 1920, [ii], **2**, 111).—According to some investigators, sodium fluoride has no action on the ordinary digestive process, but inhibits lactic, butyric, and acetic fermentation. It is suggested that the use of the salt as a preservative for butter should be permitted.

W. P. S.

Effect of Intravenous Injections of Active Deposit of Radium on Metabolism in the Dog. RUTH C. THEIS and HALSEY J. BAGG (*J. Biol. Chem.*, 1920, **41**, 525—535).—The injection was followed by an increased excretion of nitrogen, which reached a maximum figure on the second day after treatment. Urea fluctuated with total nitrogen, but there was a definite increase in excretion of ammonia and uric acid.

J. C. D.

Nutritive Factors in Plant Tissues. IV. Fat-soluble Vitamine. THOMAS B. OSBORNE and LAFAYETTE B. MENDEL [with ALFRED J. WAKEMAN] (*J. Biol. Chem.*, 1920, **41**, 549—565).—Rats

which received 0.1 gram of butter daily showed considerable ability to grow, whilst 0.5 gram per day is sufficient to restore to good nutritive condition and growth rats declining on diets deficient in the fat-soluble accessory substance. In comparison with these values, it is shown that 0.1 gram of dried tomato daily will supply all the fat-soluble factor for normal growth. Of other vegetables tested, cabbage was the least satisfactory, whereas 0.1 gram of dried lucerne, clover, timothy grass, and spinach will furnish at least as much of the vitamine as the same weight of butter.

The thermostability of the fat-soluble growth factor is discussed, and the observations of Steenbock, Boutwell, and Kent (A., 1918, i, 513) and of Drummond are not confirmed (A., 1919, i, 363).

J. C. D.

Relation between the Total Acidity, the Concentration of the Hydrogen Ion, and the Taste of Acid Solutions. R. B. HARVEY (*J. Amer. Chem. Soc.*, 1920, **42**, 712—714).—The sourness of fruit and fruit juices is shown to depend both on the hydrogen-ion concentration and on the total free acid contained in the juice. The tendency to produce hyperacidity in the ingestion of fruits is dependent on the total quantity of acid ingested, and not necessarily on the hydrogen-ion concentration alone. The addition of sugar does not affect this tendency, which, although it changes the taste, does not affect either the total acidity or the hydrogen-ion concentration.

J. F. S.

The Formation of Ferrous Sulphide in Eggs during Cooking. CHARLES KENNETH TINKLER and MARION CROSSLAND SOAR. (*Biochem. J.*, 1920, **14**, 114—119).—The discoloration on the surface of the yolk of a "hard-boiled" egg is due to the formation of ferrous sulphide, by the liberation of hydrogen sulphide from the decomposition of a sulphur compound of the egg-white and its action on the iron contained in the yolk.

J. C. D.

A Pressor Compound from the Pituitary Gland. ALBERT C. CRAWFORD (*J. Pharm. and Expt. Ther.*, 1920, **15**, 81—94).—The paper opens with a review of the literature on the active principles of the pituitary gland. The pressor substance is not extracted from the dried, powdered posterior lobes by alcohol, but is extracted by acidified alcohol. From this extract, anhydrous ether precipitates the compound as a white or slightly coloured amorphous product, which is readily soluble in water.

The fractionation of extracts prepared from the posterior lobes is described, and the preparation of a highly active pressor substance, which is precipitated by soluble mercury and silver salts, is described. No crystalline derivatives have yet been obtained.

J. C. D.

Zinc in the Human Organism. SINICHA GIAYA (*Compt. rend.*, 1920, **170**, 906—909).—The examination of the viscera of a number of corpses shows the invariable presence of zinc, the proportion

increasing with age. Thus, the amounts found varied from 0.0009% in the case of a child three months old up to 0.005% in the case of a man seventy years old. The distribution of zinc in the different organs corresponds with the following descending order: brain, lungs, stomach, liver, kidneys, intestine, heart, and spleen.

W. G.

A Case of Adipocere. G. FLORENCE (*Bull. Soc. chim. biol.*, 1919, **1**, 185—188).—A sample of adipocere gave negative tests for calcium. After removal of the fatty substances by extraction with ether, the residue contained 11.3% of nitrogen, and gave no reaction with Millon's reagent or Hopkins and Cole's reagent. It is therefore thought to be of the nature of collagen, which had escaped the transformation into fat. The author discusses the possibility of straight-chain polypeptides being converted into fatty acids, such as stearic acid, by a process of deamination and reduction.

J. C. D.

Milk as a Source of Water-soluble Vitamine. II. THOMAS B. OSBORNE and LAFAYETTE B. MENDEL [with ALFRED J. WAKEMAN] (*J. Biol. Chem.*, 1920, **41**, 515—523).—The authors have been unable to confirm in detail the classical experiments of Hopkins (*A.*, 1912, ii, 779). They find that a much larger quantity of milk than the 2 c.c. used by Hopkins is necessary to supply the vitamins required by the rat for normal growth. The discrepancy does not appear to be due to the diet of the cow from which the milk is obtained, or to the character of the inorganic constituents of the artificial ration.

J. C. D.

The Presence of Amylase in Milk and Cheese. MASAYOSHI SATO (*Biochem. J.*, 1920, **14**, 120—130).—The presence of amylase in milk, already reported by many workers, is confirmed. It is also present in commercial Cheddar cheese, although in variable amounts. Certain differences in the digestibility of various forms of starch by amylase were noted.

J. C. D.

Acidosis. XVI. The Titration of Organic Acids in Urine. DONALD D. VAN SLYKE and W. W. PALMER (*J. Biol. Chem.*, 1920, **41**, 567—585).—The organic acids present, both free and as salts, in urine are estimated by titrating between the hydrogen-ion concentrations represented by p_H 8 and p_H 2.7 respectively, after removal of phosphates and carbonates by means of calcium hydroxide. It appears that such titration represents between 95 and 100% of the organic acids present. It also includes weak bases, the dissociation constants of which fall within a range in the neighbourhood of 10^{-11} , but of this class only creatinine, and at times creatine, appear to be present in significant amounts in human urine. The average twenty-four-hour excretion of organic acids in normal young men appears to be about 5.7 to 9.8 c.c. of 0.1N-acid (uncorrected for creatinine). There appears to be little difference in the rate of excretion during day and night.

Data from cases of methyl alcohol poisoning and diabetes are examples of acidosis due to organic acids of different types. In the first case, a part of the total organic acid excretion was due to formic, lactic, and hydroxybutyric acids, but the greater part to acids of unknown nature. In diabetes, the rise in the excretion of acetone substances is so accurately paralleled by the rise in titrated organic acids that it is probable (1) that organic acids other than the acetone substances are not excreted in significant amounts in diabetic acidosis, and (2) that the easily performed organic acid titration may be used for approximate estimation of the acetone substances in diabetic urine.

J. C. D.

The Anti-scorbutic Properties of Concentrated Fruit Juices. III. ARTHUR HARDEN and ROBERT ROBISON (*Biochem. J.*, 1920, 14, 171—177).—The anti-scorbutic property of orange juice is not appreciably destroyed by evaporation to dryness under suitable conditions.

The dry residue retains considerable activity after storage for two years in a dry atmosphere at the ordinary temperature.

J. C. D.

Effect of Heat on the Anti-scorbutic Accessory Factor of Vegetable and Fruit Juices. ELLEN MARION DELF (*Biochem. J.*, 1920, 14, 211—228).—When cabbage, swede, and orange juices are subjected to temperatures up to 130°, a corresponding reduction of their anti-scorbutic properties occurs. The destruction is most marked in the case of cabbage juice, and least in the case of orange juice. The greater stability of orange juice to heat is maintained even when the juice is nearly neutralised before heating. There is evidence that growth may be affected by the limitation of the anti-scorbutic element in the diet, apart from the appearance of definite symptoms of scurvy and apart from deficiency in the other growth-promoting accessory factors.

The unexpected stability of swede and orange juice at temperatures above 100°, when the heating is conducted in the absence of air, may perhaps indicate that destruction of the anti-scorbutic factor is an oxidation process. This observation naturally has an important bearing on the canning and preserving of fruits and vegetables.

J. C. D.

Physiological Action of Fumes of Iodine. A. B. LUCKHARDT, F. C. KOCH, W. F. SCHROEDER, and A. H. WEILAND (*J. Pharm. Expt. Ther.*, 1920, 15, 1—21).—Iodine fumes may be absorbed from the human skin and appear in the urine. Iodine absorbed in this manner may actually increase the iodine content of the thyroid gland and induce a pronounced change in the histological features of that gland. The inhalation of small quantities of iodine fumes produces similar results, but larger doses may lead to respiratory disturbances and fatal acute pulmonary oedema. The administration of iodine by such inhalation is regarded as a dangerous procedure.

J. C. D.

The Formation of Acetone Substances following Ether Anæsthesia and their Relation to the Plasma Bicarbonate.

JAMES J. SHORT (*J. Biol. Chem.*, 1920, **41**, 503—513).—A study of the acetoacetic acid, acetone, and β -hydroxybutyric acid of the blood was made before and after ether anæsthesia in order to ascertain whether the formation of these substances was in any way responsible for the fall in alkaline reserve which accompanies that condition. Apparently the so-called acetone substances are not formed promptly enough during ether anæsthesia to account for the decrease in plasma bicarbonate. The analytical methods for the acetone substances (Van Slyke and Fitz, A., 1919, ii, 436) may be rendered less accurate by the presence of fat and ether, or ether alone. J. C. D.

The Minimum Concentration of $\beta\beta'$ -Dichloroethyl Sulphide (Mustard Gas) Effective for the Eyes of Man.

C. I. REED (*J. Pharm. Expt. Ther.*, 1920, **15**, 77—80).—Concentrations of 0.0005 mg. per litre of mustard gas will produce visible reactions in less than one hour of exposure in the eyes of individuals whose cutaneous resistance is relatively high. J. C. D.

Chemistry of Vegetable Physiology and Agriculture.

Action of *Bacillus fluorescens liquefaciens* (Flügge) on certain Amino-acids. A. BLANCHETIÈRE (*Bull. Soc. chim. biol.*, 1920, **2**, 29—36. Compare A., 1916, i, 699).—The amino-acids are able to act as the sole source of carbon and nitrogen for the development of this organism. The rates and degree of attack are very variable, histidine, alanine, and asparagine being particularly suitable for utilisation. Substitution of an amino-group by benzylation appears to oppose the utilisation of the amino-acid, an observation which is in agreement with the accepted theories on the decomposition of amino-acids by bacteria. The benzoyl derivatives are decomposed. J. C. D.

Influence of Reaction on Colour Changes in Tyrosine Solutions. (MRS.) ELFRIDA CONSTANCE VICTORIA VENN (*Biochem. J.*, 1920, **14**, 98—102).—Cornish and Williams showed (A., 1917, i, 613) that certain groups of bacteria isolated from discoloured Stilton cheeses are capable of producing changes of colour in media containing suspensions of caseinogen and certain amino-acids. It was found that the reaction of the media on which the organisms were grown exercised a powerful influence on the degree of discoloration. It is now shown that there is a definite range of reaction over which the organism studied is capable of producing a dis-

coloration in tyrosine solutions. A modified form of hydrogen electrode is described, which presents several advantages over many types now in use. J. C. D.

Comparative Studies on Respiration. X. Toxic and Antagonistic Effects of Magnesium in Relation to the Respiration of *Bacillus subtilis*. MATILDA MOLDENHAUER BROOKS (*J. Gen. Physiol.*, 1920, 2, 331—336).—Magnesium chloride in concentrations below 0.01M has little effect on the rate of respiration of *B. subtilis*; at 0.03M there is an increase in the rate, whilst in the higher concentrations there is a gradual decrease. There is a marked antagonism between magnesium and sodium chlorides, and a very slight antagonism between the chlorides of magnesium and calcium. J. C. D.

The Fats of Tubercle Bacilli. H. AGULHON and A. FROUIN (*Bull. Soc. chim. biol.*, 1919, 1, 176—184).—Large amounts of fatty substances may be extracted from dried tubercle bacilli by alcohol. This material is composed of fatty acids, neutral fats, esters of the higher alcohols, hydrocarbons, and a substance containing phosphorus. The latter represents about 14% of the total alcoholic extract of the organisms, and is composed of a mixture of substances of phosphatide character, which on hydrolysis yields fatty acids, glycerol, a base analogous to choline, and a gummy substance which yields dextrose. The presence of cholesterol in the extracts of the bacilli was not established. J. C. D.

Production of Formic Acid by Yeasts in Media containing Amides. P. THOMAS (*Ann. Inst. Pasteur*, 1920, 34, 162—176. Compare this vol., i, 126).—The volatile acidity produced during the culture of yeast on media containing acetamide is in part due to the formation of formic acid and in part due to the formation of acetic acid, the relative proportions of these two acids varying with the conditions. The presence, in addition, of various ammonium salts has a very marked effect on the total volatile acidity and the relative amounts of the two acids produced. In the presence of ammonium sulphate, oxalate, succinate or hydrogen carbonate the volatile acid produced is almost entirely formic acid, whilst in the presence of ammonium aspartate the two acids are produced in almost equal amounts.

The author discusses the various theories put forward to explain the formation of acetic acid, and concludes that the mechanism is not a simple one, but that there are several phenomena, which will function according to the conditions and may replace or superpose on one another, as the conditions vary. W. G.

Alteration in the Inverting Power of Top Yeast by Pre-treatment. STURE LÖVGREN (*Fermentforsch.*, 1920, 3, 221—240; from *Chem. Zentr.*, 1920, i, 473—474).—The experiments were undertaken with the object of determining the influence of the inorganic constituents on the formation of saccharase and

the differences between their action on bottom yeast, which has generally been used previously by Euler and his co-workers, and on top yeast. Pre-treatment of the yeast was effected with sugar, ammonium acetate, magnesium chloride or sulphate, calcium chloride, potassium chloride, sodium chloride, potassium dihydrogen phosphate, yeast water, alcohol, acetone, or carbamide, sometimes singly and sometimes in combinations. The results are summarised in the following statements: (1) The neutral salts investigated do not appear to have any actual influence on the variation of the inverting power of the types of top yeast used, either in small amounts at the ordinary temperature or in larger quantities at the ordinary or higher temperature. (2) Certain experiments indicate that the inverting power of top yeast may be distinctly increased by suitable pre-treatment. Addition of nitrogenous nutriment is advantageous, but not essential. In the first twenty-four hours (of fermentation) the inverting power increases slowly or may even decrease; after cessation of fermentation, it increases gradually at first, then more rapidly to a maximum, at which it remains for a time, and then slowly decreases again. The curves are more or less flattened according to the properties of the original yeast. (3) One experiment shows that top yeast is much less suitable for enrichment experiments of this kind than bottom yeast. (4) The inversion constants of the original yeasts varied between 20 and 40, with a mean value (from nine estimations) of 28 per gram of yeast (30% dry substance) and 9.6 grams of sucrose at 16°, from which the constant 3×10^{-12} is calculated. (5) If the increase of inverting power is considered to be a consequence of augmented vitality due to the pre-treatment, the nitrogen nutriment must be regarded as essential. The fact that a marked increase can occur without administration of nitrogen is probably explained by the formation of the necessary amount of the latter by autolysis. H. W.

Activation of Living Yeast by Yeast Extract and by Salts of Organic Acids. HANS VON EULER (*Zeitsch. techn. Biol.*, 1919, 7, 155—164; from *Chem. Zentr.*, 1920, i, 473).—I. *Activation of Living Yeast by Yeast Extract or Preparations of Yeast Extract.*—In connexion with the investigations of Euler and Berggren (A., 1913, i, 145) and Harden and Young (A., 1914, i, 237), the author adduces new evidence to show that alcoholic fermentation by fresh top-yeast is greatly accelerated by activators, presumably co-enzymes, which are present in aqueous yeast extract, and that the phenomenon is observed when the number of cells in the fermenting liquor undergoes no, or very slight, increase. The activation of dry yeast by the co-enzyme is almost independent of the acidity of the solution in the region $P_H=3-7$.

II. *Activation of Living Yeast by Salts of Organic Acids.*—In contrast to Harden and Young, the author finds that the increase in the number of cells due to the addition of alkali formate never exceeds the experimental error involved in counting. On the other hand, it is shown that alcoholic fermentation by fresh top-yeast is greatly accelerated by ammonium or alkali formate. H. W.

Regeneration of Saccharase in Pre-treated Yeast. HANS VON EULER and OLOF SVANBERG (*Zeitsch. techn. Biol.*, 1919, 7, 165—172; from *Chem. Zentr.*, 1920, i, 473).—The authors have investigated the length of period necessary for the re-formation of enzyme-content removed by previous treatment; the results so far obtained do not permit a definite conclusion to be drawn. H. W.

Ferment Action. VI. A. FODOR (*Fermentforsch.*, 1920, 3, 193—200; from *Chem. Zentr.*, 1920, i, 471—472. Compare Abderhalden and Fodor, A., 1919, i, 369).—An active colloidal mixture can be separated from yeast extract by the addition of twice its volume of absolute alcohol; the precipitate (*R*) is separated after twelve hours and thoroughly washed with alcohol. It is not completely dissolved by protracted treatment with water at 37°, but leaves a residue (*r*), which yields a clear, golden-yellow solution with dilute sodium hydroxide, from which it does not separate on treatment with excess of acid. Whilst *R* contains the colloids of yeast extract, the aqueous-alcoholic filtrate is free from them, and is completely inactive fermentatively. The aqueous extract from *R* is readily coagulated when heated and, when cautiously acidified, deposits a perfectly white precipitate. It causes the fission of glycyl-*l*-leucine, but its activity is small in comparison with that of the original yeast extract. The solution also contains magnesium and phosphoric acid ions and, when rendered alkaline with sodium hydroxide, gives a crystalline precipitate of magnesium sodium phosphate and some magnesium ammonium phosphate in the same manner as the original extract. The residue, *r*, consists mainly of denatured proteins which are precipitated when the solution in alkali is acidified (owing to the action of the salt). According to the nitrogen content, this product differs from that precipitated by acids from the aqueous extract of *R*, though each is to be regarded as a nucleoprotein.

If alcohol is added to the yeast extract after removal of phosphate by addition of alkali, a precipitate, *R*₁, is obtained, which leaves a residue, *r*, after treatment with water. The faintly alkaline aqueous filtrate is not noticeably coagulated by heat even after neutralisation, yields at most an opalescence when cautiously acidified with hydrochloric acid, and is completely inactive towards glycyl-*l*-leucine even after addition of magnesium phosphate solution, the favourable influence of which on fermentative activity has been frequently demonstrated. The product, *r*₁, closely resembles *r*, and has the same nitrogen content. In the dry condition neither can function as acid or base in the sense of the ionic theory, though each acquires this property after hydration and increase of surface, which slowly occurs under the influence of acid or alkali. If more concentrated alkali hydroxide is used in reprecipitation, elimination of phosphoric acid occurs, even to such an extent that the substance becomes free from phosphorus; the nitrogen content is simultaneously altered.

In connexion with the present and previous investigations, the development of ferment action is explained on a colloidal chemical

basis. The union of the ferment, a negatively charged colloid, by adsorption with the substrate, activates the elements necessary for the hydrolysis of the latter by bringing them into the ionic condition. This happens as a consequence of the partial diminution of the adsorption potential of the colloidal particles by the opposite charge of the substrate. The optimal hydrogen-ion concentration depends on the individual properties of the ferment colloids and the amphoteric substrate and their mutual relationships. In the case of ferments which are active in alkaline solution, this becomes more displaced towards the alkaline side as the difference in acidic nature between the colloid and the substrate increases. H. W.

The Products of the "Acetone-*n*-Butyl Alcohol" Fermentation of Carbohydrate Material, with Special Reference to some of the Intermediate Substances Produced. JOSEPH REILLY, WILFRED JOHN HICKINBOTTOM, FRANCIS ROBERT HENLEY, and AAGE CHRISTIAN THAYSEN (*Biochem. J.*, 1920, **14**, 229—251).—In a normal fermentation of maize mash the acidity rises until a maximum is reached from thirteen to seventeen hours after inoculation. After this point is reached there is a very marked acceleration in the rate of production of acetone, *n*-butyl alcohol, carbon dioxide, and hydrogen, the acidity falling gradually to a constant value. The greater part of the acids produced are volatile in steam, and butyric and acetic acids were identified in the distillate. These acids are probably intermediate products in the production of acetone and butyl alcohol. Evidence in support of this is given by the results of carrying on the fermentation in the presence of calcium carbonate, when practically no acetone or butyl alcohol was obtained.

When acetic acid or ethyl acetoacetate is added to the fermenting mash an increased yield of acetone is obtained. Addition of formic acid and trichloroacetic acid appeared to inhibit fermentation, whilst propionic and butyric acids are converted into the corresponding alcohols.

A tentative suggestion of the action is put forward, in which acetic acid is considered as a monoketide, $\text{H}\cdot\text{CH}_2\cdot\text{CO}\cdot\text{OH}$. By condensation $\text{CH}_3\cdot\text{CO}$ yields $\text{CH}_3\cdot\text{C}(\text{OH})\cdot\text{CH}\cdot\text{CO}$, which by elimination of CO_2 and the addition of the elements of water would yield acetone. Similarly, the increased yield of acetone from acetoacetic acid may be explained on the assumption that this substance possesses the structure of a diketide. This hypothesis may be extended and is capable of explaining ordinary alcoholic fermentation. No direct evidence was obtained of the formation of acetaldehyde or of formic acid as an intermediate product in the acetone fermentation.

J. C. D.

Influence of a Reduced Amount of Potassium on the Physiological Characters of *Sterigmatocystis nigra* [*Aspergillus niger*]. M. MOLLIARD (*Compt. rend.*, 1920, **170**, 949—951).—When all but one-eightieth of the potassium phosphate

in the normal culture medium is replaced by sodium phosphate, the growth of *Aspergillus niger* is very slow and the yield of mycelium is very small. The sugar is to a large extent oxidised, but instead of giving almost entirely carbon dioxide, an important amount of oxalic acid is formed, the amount increasing regularly so long as there is any sugar left in the culture medium. Other points noted are the more rapid disappearance of the dextrose than of the levulose, the total absence of conidia and of the black pigment, formation of a golden-yellow pigment diffusing into the medium, and the production of a substance soluble in the culture solution and giving a blue colour with iodine.

W. G.

The Utilisation of α -Methylglucoside by *Aspergillus niger*. ARTHUR W. DOX and G. W. ROARK, jun. (*J. Biol. Chem.*, 1920, **41**, 475-481).—*Aspergillus niger* grows very poorly on media containing α -methylglucoside as the only source of carbon, but readily on sucrose media in the presence of the glucoside. More rapid utilisation of the glucoside occurs on the sucrose-free medium when the culture inoculated is a vigorous one, or one which has previously been growing in the presence of both sucrose and the glucoside. A gradual cumulative adaptation could not be demonstrated with certainty.

J. C. D.

Synthesis of Aromatic Amino-acids in the Living Cell. L. HUGOUNENQ and GABRIEL FLORENCE (*Bull. Soc. chim. biol.*, 1920, **2**, 13-18).—*Aspergillus niger* produces proteins containing the aromatic amino-acids when growing on culture media containing inorganic nitrogen, sucrose, and tartaric acid. It is possible that it is able to utilise the carbon chain of a pentose for these synthetic processes. Probably the products of assimilation are broken down into substances of small molecular dimensions before the synthetic processes are commenced, and a parallel is drawn with the metabolic and anabolic processes in the higher animals.

J. C. D.

Photo-synthesis in Fresh-water Algæ. I. The Fixation of Both Carbon and Nitrogen from the Atmosphere to Form Organic Tissue by the Green Plant Cell. II. Nutrition and Growth Produced by High Gaseous Dilutions of Simple Organic Compounds, such as Formaldehyde and Methyl Alcohol. III. Nutrition and Growth by means of High Dilutions of Carbon Dioxide and Oxides of Nitrogen without Access to Atmosphere. BENJAMIN MOORE and T. ARTHUR WEBSTER (*Proc. Roy. Soc.*, 1920, [B], **91**, 201-215).—Experimental evidence is given in support of the view that the lowest type of synthesising cell existing, namely, the unicellular alga, possesses the power of fixing carbon and nitrogen and building these up into reduced organic compounds with uptake of energy, the source of the energy being the sunlight. It is shown that formaldehyde or methyl alcohol fed to such a

cell at a sufficiently high dilution can be used as a nutrient source of carbon in absence of carbon dioxide, and very marked growths have been obtained with these substances as the sole source of carbon. In the absence of all other sources of nitrogen except the atmospheric nitrogen, but with abundance of carbon dioxide, the unicellular algæ can fix nitrogen, grow, and form proteins. The rate of fixation and growth is, however, greatly accelerated if nitrites or oxides of nitrogen are available, and the latter may be supplied in the gaseous form from the atmosphere. W. G.

The Inhibition of Invertase in the Sap of *Galanthus nivalis*. T. G. MASON (*Sci. Proc. Roy. Dubl. Soc.*, 1920, 16, 83—97).—Experiments with the sap of the leaves of *Galanthus nivalis*, extracted under varying conditions, indicate that factors inhibiting the activity of the invertase may be present in the sap. Changes of a nature not yet clearly understood occur in the sap after its extraction from the leaf, which lead to a clumping of the colloids, and possibly the enzyme may be inactivated by adsorption on the coagulated colloids. W. G.

Presence of Gentianose and Sucrose in various Gentians. MARC BRIDEL (*J. Pharm. Chim.*, 1920, [vii], 21, 306—311; *Bull. Soc. chim. biol.*, 1920, 2, 37—41). Compare A., 1913, i, 149, 434, 690).—The author has detected the presence of both gentianose and sucrose in the roots of *Gentiana cruciata* and *G. purpurea*. The reversible change between gentianose and sucrose is governed by the activity of the enzyme gentiobiase. W. P. S.

Anthocyanins. I. The Anthocyanins of the Young Leaves of the Grape Vine. OTTO ROSENHEIM (*Biochem. J.*, 1920, 14, 178—188).—The red pigment of the young leaves of the grape vine is probably identical with oenidin, the anthocyanidin derived from the pigment of the purple grape. This is the first case which has been noted in which the red pigment of the leaves is a free anthocyanidin, and the European species *Vitis vinifera* appears to be the only representative of the family *Vitis* which is so characterised. The occurrence of a colourless modification of the pigment was demonstrated, for which the general name *leucoanthocyanin* is proposed. It is present in combination possibly with carbohydrate, and is converted into anthocyanidin by strong acids. J. C. D.

Distribution of Lycorine in the N.O. Amaryllidaceæ. K. GORTER (*Bull. Jard. bot. Buitenzorg*, 1920, [iii], 1, 352—358).—The first accurate description of an alkaloid of this order refers to lycorine from *Lycoris radiata*, Herb. (Morishima, A., 1899, i, 92), and this is identical with narcissine (Ewins, T., 1910, 97, 2406) from *Narcissus pseudonarcissus*, L. (compare Asahina and Sugii, A., 1913, i, 1093). The latter name should therefore be abandoned; the formula of the alkaloid is $C_{16}H_{17}O_4N$ (Ewins), with which the analytical results of Morishima agree better than with

the formula $C_{33}H_{33}O_8N_2$ proposed by him, which is, moreover, excluded by molecular-weight determinations (Ewins, Asahina, and Sugii). The alkaloid of *Buphane disticha*, Herb. (Tutin, T., 1911, 99, 1240) is also lycorine, as is that in *Narcissus Tazetta*, L. (Yamanouchi, *Arch. Pharm.*, 1913, 251, 357). Gorter has further found lycorine in *Zephyranthes rosea*, Lindl., *Crinum asiaticum*, L., *C. giganteum*, Andr., *C. pratense*, Herb., *Hymenocallis littoralis*, Salisb., *Eucharis grandiflora*, Planch., and *Eurycles sylvestris*, Salisb. *Crinum* spp. contain most (0.1—0.18% of bulb). G. B.

A New Plant containing Coumarin: *Melittis melissophyllum*, L. P. GUÉRIN and A. GORIS (*Compt. rend.*, 1920, 170, 1067—1068).—The leaves of *Melittis melissophyllum*, L. contain coumarin apparently in the form of a glucoside decomposable by emulsin. The coumarin may be extracted along with quercetin from the dried leaves by 95% alcohol. W. G.

Constituents of *Morinda citrifolia*. JOHN LIONEL SIMONSEN (T., 1920, 117, 561—564).

Acidity and Acidimetry of Soils. I. Studies of the Hopkins and Pettit Method for Estimating Soil Acidity HENRY G. KNIGHT (*J. Ind. Eng. Chem.*, 1920, 12, 340—344).—Investigation of this method (extraction with potassium nitrate solution and titration of the extract) showed that an acid soil gives the same acidity whether it is extracted with *N*/1-potassium nitrate, potassium chloride, sodium nitrate, sodium chloride, or calcium chloride solution. The acidity of the salt extract of an acid soil is independent of the temperature within the range of 25° to 90°, but the acidity of the first portions of the extract increases with increase of the concentration of the salt solution. The difference in absorption of calcium and potassium from solutions of their bases by an acid soil may be due to precipitation. There is a basic exchange when a salt solution is added to an acid soil; alumina is dissolved, but this does not account for the total acidity of the solution. Exchange of acid radicles is slight or does not occur. W. P. S.

Hysteresis of Aqueous Suspensions of Humus Earth. HEINRICH PUCHNER (*Kolloid Zeitsch.*, 1920, 26, 159—168. Compare this vol., i, 274).—A continuation of the previously published work. The present paper deals particularly with hysteresis phenomena occurring in the insoluble portion obtained from the settling of suspensions of peat in water. It is shown that the delayed effects observed are due, not only to physical and chemical processes, but are very largely influenced by the growth of low forms of plant life. J. F. S.

General and Physical Chemistry.

Refraction and Dispersion of Carbon Dioxide, Carbon Monoxide, and Methane. CLIVE CUTHBERTSON and MAUDE CUTHBERTSON (*Proc. Roy. Soc.*, 1920, [A], **97**, 152—159).—The refractivities and dispersion coefficients of the three gases were determined with a Jamin refractometer. For the green mercury line ($\lambda = 5461$), the refractivities, reduced to 0° and 76 cm., were as follows: carbon dioxide, 4505; carbon monoxide, 3364; methane, 4415. In all cases, the value of $(\mu - 1) \cdot 10^7$ is given. Tables giving the dispersion are supplied. The refractions and dispersions of the carbon atom calculated from the results do not show any agreement, the figures for the relative numbers of electrons and the free frequencies being also discordant. It is concluded that the forces which control the motion of a dispersion electron in an atom are profoundly affected by the proximity of another atom in combination with it. If the two atoms are of the same element, as in the molecules of diatomic gases, a similar, but probably simpler, change occurs in such a way that the free frequencies in both atoms are originally the same and are altered to the same extent.

J. R. P.

The Variation with Pressure of the Wave-length of the Rays of the Bands of Cyanogen. A. PEROT (*Compt. rend.*, 1920, **170**, 988—990).—By varying the pressure from atmospheric pressure down to 2—3 cm. of mercury, it is shown that the values of $d\lambda/\lambda$ for the bands 4197 and 3883 are 1.8×10^{-6} and 1.4×10^{-6} respectively.

W. G.

Spectrum of Copper. W. M. HICKS (*Phil. Mag.*, 1920, [vi], **39**, 457—481).—A theoretical paper in which the copper spectrum is treated in the same way as the spectra of silver and gold (A., 1919, ii, 441). Strong, well-defined sets are given for the orders $m = 2, 3$ in both the *S* and *D* sets and for the first order of *P*. Those for *S* (2) are in the red and in step with those of silver. The others show the Zeeman patterns proper for their respective types. These may therefore be adopted definitely as normal series lines. In the higher orders, the intensities fall off more rapidly and irregularly than usual, and there is also evidence for numerous displacements. These are apparently the cause of the low intensities and the large number of weak lines. In consequence, the determination of the *S* and *D* limits, with any exactness, from the series lines alone is rendered impossible.

J. F. S.

Effect of Solvent on the Ultra-violet Absorption Spectrum of a Pure Substance. F. O. RICE (*J. Amer. Chem. Soc.*, 1920, **42**, 727—735).—The effect of the solvents, water, ethyl alcohol, heptane, and chloroform, on the ultra-violet absorption spectrum

of many ketones has been investigated. It is shown that all aliphatic ketones, except acetone and methyl ethyl ketone, follow Beer's law, that is, the molecular extinction is independent of the concentration and solvent. With acetone and methyl ethyl ketone there are deviations when ionising solvents are used, due to partial disruption of the associated molecules. Kundt's rule, which states that with increasing refractivity of solvent the absorption band moves towards the red, holds good if it is regarded as a rough generalisation. When a pure substance is dissolved in an ionising solvent, the absorption centre moves towards the ultra-violet; if a pure substance is dissolved in a neutral, non-ionising solvent, the absorption centre is unaffected or moves toward the red end of the spectrum. It is probable that this is a general rule which holds for all classes of absorbing substances. J. F. S.

Light Absorption and Fluorescence. V. The so-called Molecular Rotational Frequencies of Water. E. C. C. BALY (*Phil. Mag.*, 1920, [vi], **39**, 565—577. Compare A., 1916, ii, 363).—A theoretical paper in which, from the atomic frequency of oxygen, 2.4531×10^{11} , found by the author for this substance in sulphur dioxide (*loc. cit.*), and the measurements of Sletor (*Astrophys. J.*, 1918, **48**, 125), the author is able to calculate the central frequencies of the water absorption bands. The agreement between the calculated values and the values observed by Sletor is good, the maximum difference being 0.0022μ , whilst the average difference is $\pm 0.00074 \mu$. The results obtained for the system of frequencies possessed by the molecules of sulphur dioxide and water definitely establish the existence of simple relationships between the three sets of frequencies, molecular, intramolecular, and atomic. The atomic frequencies are characteristic of the individual atoms, the molecular frequencies are characteristic of the molecule as a whole, and the intramolecular frequencies are characteristic of groups of atoms in the molecules. J. F. S.

Activation of Hydrogen Peroxide by Light. HARRY A. CURTIS (*J. Amer. Chem. Soc.*, 1920, **42**, 720—724).—Solutions of aniline-green and magenta are not bleached when exposed to the light of a quartz mercury lamp, neither are they bleached by the addition of 3% hydrogen peroxide to them until the mixture is exposed to the light. The rate of bleaching of the mixtures was followed by means of a Hellige-Leitz colorimeter, and curves are given. To be sure that the bleaching in light was due to hydrogen peroxide and not to ozone, solutions of the dyes were submitted to the light while a stream of oxygen was bubbled in; there was no bleaching in this case. Hence it appears that the oxidising power of hydrogen peroxide with respect to the bleaching of dyes is increased by exposing the mixture to light of short wave-lengths. J. F. S.

Chemical Induction in Photographic Development. I. Induction and the Watkins Factor. S. E. SHEPPARD and G. MEYER (*J. Amer. Chem. Soc.*, 1920, **42**, 689—700).—The Lainer

effect, acceleration of development of photographic plates by dilute solutions of iodides, has been investigated, and shown to affect chiefly organic developers of low reduction potential, such as quinol. It is also shown that the principal effect is to overcome the induction with such organic developers, consequently increasing the Watkins factor. The effect is regarded as due to the increased adsorption and complex formation between silver haloid and developer. The bearing of this on the theory of development is discussed. There is, in addition, a fogging action by dilute solutions of potassium iodide on silver bromide emulsions, which is attributed to nucleus infection of the grain. J. F. S.

Stereoisomeric Transformations and Polymerisation of Organic Substances under the Influence of Light and their Constitution. P. R. KOGEL (*Photo. Korr.*, 1919, 56, 368—380; from *Chem. Zentr.*, 1920, i, 489).—The acetylene and cyanogen groups are photopolymeric. The methyl group with a double bond (ethylene group) is both photostereoisomeric and photopolymeric. The same is true of the corresponding compounds of nitrogen. The orthoquinonoid formula is assigned to anthracene on account of its ability to undergo polymerisation. The sensitiveness of diazonium compounds to light depends on their tendency to photostereoisomeric transformation. The disposition of the chief valencies in the stereoisomeric and polymeric methyl group is the same as that in the pallidogenic methyl group. H. W.

Photosynthesis and the Electronic Theory. HENRY H. DIXON and HORACE H. POOLE (*Sci. Proc. Roy. Dubl. Soc.*, 1920, 16, 63—77).—Electrical measurements made with metallic plates coated with chlorophyll in different ways and illuminated from different sources of light indicate that those wave-lengths of light which are effective in photosynthesis are unable, to any appreciable extent, to expel electrons from the leaf pigment complex, and hence cannot in this way produce ionisation or bring about reactions external to the pigment. The action apparently occurs within the molecule of the chlorophyll itself, the atomic groups of the leaf pigment entering into the action of photosynthesis and participating in the combinations and decompositions which ultimately lead to the formation of carbohydrates and the evolution of oxygen. W. G.

The Scattering of γ -Rays. K. W. FRITZ KOHLRAUSCH (*Physikal. Zeitsch.*, 1920, 21, 193—198).—A pencil of γ -rays, from 0.8 gram of radium chloride, after passing through absorption screens, falls on a block of carbon, aluminium, zinc, tin, or lead as radiator at 0.5 metre distance, and the secondary γ -radiation at different angles α with the direction of incidence is examined as regards intensity and penetrating power over a circle of 0.64 metre radius, by means of an ionisation chamber. The decrease of the hardness and intensity of the secondary γ -radiation with increasing

values of a was confirmed. The change of hardness was shown to be due to the existence in varying proportion of two types of secondary rays, S_1 and S_2 , corresponding with the two types of primary, K_1 and K_2 . The results showed that S_1 was a scattered K_1 radiation of the same hardness, and that probably S_2 is similarly a scattered K_2 radiation. None of the S_1 radiation is scattered through more than 90° , but the S_2 radiation extends in the direction of incidence as well as in that of emergence. Tables are given showing the distribution of the intensity of the radiation over the complete circle, and the results are compared with the theory of Debye and shown to be in qualitative agreement with it, particularly as regards the asymmetry of distribution found for the radiation in the directions of incidence and emergence. The probable wave-length of the γ -rays is discussed in the light of these results.

F. S.

The Properties of Reinforcing Screens with respect to X-ray Spectra, and a Decomposition of the β -Line of the K Spectrum of Tungsten. MAURICE DE BROGLIE (*Compt. rend.*, 1920, 170, 1053—1056).—The effect of reinforcement increases rapidly with the penetration of the rays, and the luminous excitation of the screen is thus itself dependent on the absorption band of the heavy metal (tungsten in the calcium tungstate used) which the screen contains. With a screen coated with cadmium tungstate there was no apparent selective reinforcement due to the cadmium.

Using special conditions to obtain the K spectrum of tungsten it was found that the line β_1 , $\lambda = 0.1844$ Ångström, was split into two components, the one with the greater wave-length being the more feeble. The difference between these two components is given by $d\lambda = 0.0007$ Ångström.

W. G.

Mass-spectra of Chemical Elements. F. W. ASTON (*Phil. Mag.*, 1920, [vi], 39, 611—625).—A full account is given of the structure and method of operating a positive ray spectrograph, which is capable of producing a focussed positive ray spectrum (mass spectrum). The results of a provisional analysis of eleven chemical elements, hydrogen, helium, carbon, nitrogen, oxygen, neon, chlorine, argon, krypton, xenon, and mercury are summarised. These show that only five—hydrogen, helium, carbon, nitrogen, and oxygen—are “pure” elements, the others being composed of various numbers of isotopic constituents. The number of isotopes n and their masses m in order of intensity are: hydrogen, $n=1$, $m=1.008$; helium, $n=1$, $m=4$; carbon, $n=1$, $m=12$; nitrogen, $n=1$, $m=14$; oxygen, $n=1$, $m=16$; neon, $n=2$, $m=20, 22$ (21); chlorine, $n=2$, $m=35, 37$ (39); argon, $n=(2)$, $m=40$ (36); krypton, $n=6$, $m=84, 86, 82, 83, 80, 78$; xenon, $n=5$, $m=(128, 131, 130, 133, 135)$; mercury, $n=(5)$, $m=(197—200, 202, 204)$. The values enclosed in brackets are provisional. With the exception of those due to H_1 , H_2 , and H_3 , all masses measured, allowing for multiple charges, are exactly whole numbers within the error of experiment ($O=16$). The lines due to hydrogen indicate that the

mass of this element is greater than unity on this scale, and is in good agreement with the chemical value 1.008. J. F. S.

The Determination of the Radioactivity of Spring Waters. OTTOMAR NÜRNBERGER (*Physikal. Zeitsch.*, 1920, 21, 198—203).—A comparison of the different methods and instruments used by H. W. Schmidt, Engler and Sieveking, Mache and Meyer, Kohlrausch and Loewenthal, for the estimation of the radium emanation in spring waters, and the conditions to be observed to obtain trustworthy and comparable results. F. S.

Course of the Transformation Process of Isomeric Ions. GEORG VON HEVESY and LÁSZLÓ ZECHMEISTER (*Zeitsch. Elektrochem.*, 1920, 26, 151—153).—It is shown by the radioactive indicator method that a dynamic equilibrium exists between bivalent and quadrivalent lead ions in glacial acetic acid solution, and in consequence it follows that electrons can pass of themselves, in certain circumstances, from one ion to an isomeric ion and also to an electrode. J. F. S.

Ionisation and Activity of Largely Ionised Substances. ARTHUR A. NOYES and DUNCAN A. MACINNES (*J. Amer. Chem. Soc.*, 1920, 42, 239—245).—A theoretical paper in which the experimental results of MacInnes and Parker (A., 1915, ii, 510, 734), Ellis (A., 1916, ii, 369), and Noyes and Ellis (A., 1918, ii, 27), in connexion with the electrodes $\text{Ag} + \text{AgCl} | \text{LiCl} | \text{LiHg} | \text{LiCl} | \text{AgCl} + \text{Ag}$ and $\text{Hg} + \text{HgO} | \text{KOH} | \text{K}$ in $\text{Hg} | \text{KOH} | \text{HgO} + \text{Hg}$ are discussed. It is shown that in the case of potassium chloride, lithium chloride, hydrochloric acid, and potassium hydroxide the activity coefficient decreases with increasing concentration much more rapidly than does the conductivity-viscosity ratio, the differences amounting to from 7% to 15% at $N/10$ - and from 5% to 18% at $N/5$ -concentration. In the case of all the substances except potassium chloride, the activity-coefficient, unlike the conductivity-viscosity ratio, passes through a pronounced minimum in the neighbourhood of $N/5$ and afterwards increases rapidly at the higher concentrations. Even potassium chloride, according to Harned's data (A., 1918, ii, 597), has a minimum activity-coefficient about $2N$. The activity-coefficient even at moderate concentrations varies considerably with the nature of the substance; thus its value in $0.5N$ -potassium chloride is 65%, lithium chloride 73%, hydrochloric acid and potassium hydroxide 77%. Thus it follows that the conductivity ratio can no longer be regarded as even an approximate measure of the activity of the ions of highly ionised substances in their mass action and thermodynamic relations. The activity varies with the concentration differently in the case of different substances and, at present, it can only be determined empirically for each substance with the aid of chemical equilibrium measurements, *E.M.F.*, and freezing-point measurements. It is also shown that the ionic activity-coefficients cannot be proportional to or mainly determined by the fraction of

the substance ionised; for this fraction could not increase with increasing concentration unless the ionising power of the medium becomes much greater at moderate concentrations, and even then it could not become greater than unity, as is actually the case with the activity-coefficient of hydrochloric acid in concentrations above $2N$.
J. F. S.

The Constancy of Electrical Conductivity of Gases during Chemical Reactions. MAX TRAUTZ and FRIEDRICH AUGUST HENGLEIN (*Zeitsch. anorg. Chem.*, 1920, 110, 237—289).

—To determine whether or no ionisation occurs during chemical reactions, a number of purely gaseous reactions were studied. The apparatus used consisted essentially of a glass reaction vessel of cylindrical form containing a cylindrical condenser, both surfaces of which were of graphite or glass. The outer surface was connected by a platinum wire sealed into the wall of the reaction vessel to a high-tension battery, the inner surface similarly to a quadrant electrometer set. Preliminary experiments showed that none of the materials employed, matte glass surfaces, platinum wire, graphite or paraffin, had any appreciable influence on the velocity of the reaction $2NO + Cl_2 = 2NOCl$. When the reaction vessel was filled with dry air and the outer electrode connected to the high-tension battery, a small charge appeared on the inner electrode and increased gradually to a maximum value, in spite of the most careful insulation of the two electrodes. This charge, it was proved, is a result of the ionisation of the gas. It increases with increasing pressure and is greater for chlorine than for air. The ionisation of the air in the enclosed vessel was considerably greater than that which has been found by other methods for free atmospheric air.

The reactions studied were the following: $2NO + Cl_2 = 2NOCl$; $2NO + Br_2 = 2NOBr$; $2HBr + Cl_2 = 2HCl + Br_2$; $Cl_2 + H_2 = 2HCl$. In no case could evidence of ionisation during the reaction be obtained. Pinkus stated (*A.*, 1918, ii, 286) that ionisation could be detected in the case of the first reaction when chlorine was in excess. His results could not be confirmed, and were probably due to frictional electricity generated by the sudden rush of gas into the reaction vessel. It is concluded that during gaseous reactions at moderate temperatures, even when the heat of reaction is great, no free electrons are produced.

Manometric experiments were made to determine whether, when gaseous hydrogen chloride, bromide, or iodide is mixed respectively with gaseous chlorine, bromine, or iodine, any hydrogen trihaloid is formed. The results in each case were negative. E. H. R.

Disruptive [Sparking] Potential in Carbon Dioxide at High Pressures. C. E. GUYE and P. MERCIER (*Arch. Sci. phys. nat.*, 1920, [v], 2, 30—49, 99—124).—The authors measured the sparking potential in carbon dioxide at high pressures with great accuracy. At atmospheric pressure, with plane electrode

45 mm. diameter, the sparking potential for the same distance is greater in air than in carbon dioxide, although this difference appears to vanish at small distances. Exposure to ultra-violet light diminishes the potential to a greater extent in carbon dioxide than in air. The action of ultra-violet light is inappreciable at pressures greater than 10 atm. For distances from 2 to 5 mm. the potential increases linearly with the pressure up to 10 atm. For 1 mm., and especially for 0.5 mm., this relation no longer holds, although the deviations are very small. The results depend on the form of the electrodes. The results are explained by an accumulation of positive and negative ions in the vicinities of the electrodes before the spark passes. This leads to the deviation from Paschen's law at small distances, and also causes the energy of the spark to increase, giving rise to a more intense spark.

J. R. P.

Absorption of Gases in the Electric Discharge Tube.

F. H. NEWMAN (*Proc. Physical Soc.*, 1920, **32**, 190—195. Compare A., 1914, **ii**, 703).—A continuation of experiments previously described (*loc. cit.*). Nitrogen is absorbed by both sodium and potassium under the influence of an unidirectional discharge in a discharge tube. The experiments were made at various pressures (8.1—1.0 mm.), and with the metals as cathode and anode respectively. In the case of sodium, it is shown that the amount of absorption is greater when it is the cathode. In the case of potassium, less gas is absorbed than with sodium. Using the liquid alloy of sodium and potassium, there was no difference in the rate of absorption when the temperature was raised from 50° to 200°, but above this temperature the rate of absorption increased very much. After the discharge had been interrupted and the alloy was heated to above 300°, there was no evolution of gas, so that in all probability moderately stable nitrides of sodium or potassium, or both, had been formed.

J. F. S.

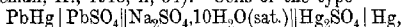
Reproducible Liquid Junction Potentials: The Flowing Junction.

ARTHUR B. LAMB and ALFRED T. LARSON (*J. Amer. Chem. Soc.*, 1920, **42**, 229—237).—The reproducibility and constancy of liquid junction potentials has been investigated in the case of gelatin diaphragm, parchment diaphragm, and flowing junctions. The experiments show that liquid junctions formed between the bearing surfaces of ground-glass stoppers, in gelatin diaphragms, and in parchment paper diaphragms with 0.1*N*-hydrochloric acid and potassium chloride solutions are not constant and reproducible to closer than 0.2—0.4 millivolt. Somewhat more constant results are obtained with parchment diaphragms on stirring. Fresh junctions in 5 mm. tubes give potentials reproducible in 0.1*N*-solutions to about 0.03—0.06 millivolt when the electrolyte is prevented from oscillating, but with *N*-solutions variations of 0.3 millivolt occur. Stirred junctions sometimes give very constant potentials, but these are quite different from that produced by a flowing junction, and, moreover, they differ, depend-

ing on the method of stirring. A flowing junction, obtained simply by an upward current of the heavier electrolyte meeting a downward current of the lighter electrolyte in a vertical tube at its point of union with a horizontal outflow tube, or by allowing the lighter electrolyte to flow constantly into a large volume of the heavier electrolyte, even with *N*-solutions, gives potentials constant and reproducible to 0.01 millivolt. An apparatus in which such flowing junctions may be obtained is depicted in the paper.

J. F. S.

A Lead Standard Cell. M. G. MELLON and W. E. HENDERSON (*J. Amer. Chem. Soc.*, 1920, **42**, 676—689. Compare Henderson and Stegeman, A., 1918, ii, 54).—Cells of the type



of which the *E.M.F.* and stability have previously been studied (*loc. cit.*), were constructed, in which the electrolyte was replaced by solutions, both saturated and unsaturated, of the sulphates of potassium, lithium, magnesium, nickel, cobalt, zinc, manganese, cadmium, and copper. These cells have been examined with respect to their *E.M.F.*, reproducibility, and constancy. It is shown that the cell with sodium sulphate, constructed, in 1917 (*loc. cit.*), has the same value as freshly made cells. It is shown that saturated cells containing the sulphates of nickel, cobalt, zinc, or manganese are substantially as reproducible and as constant as those containing sodium sulphate. This constancy is usually reached in four to five days after preparation, and these cells appear to possess the characteristics necessary for a standard cell. The *E.M.F.* of the cell which has become constant seems to be nearly independent of the soluble sulphate used. The value of the *E.M.F.* for cells containing sodium or nickel sulphate is practically the same, 0.96466 volt and 0.96430 volt respectively, whilst those of cells containing cobalt, zinc, and manganese sulphate are very close together, but are slightly higher than those of the first-named cells; they have values 0.96478, 0.96477, and 0.96478 volt respectively. Saturated cells containing the sulphate of lithium, magnesium, or cadmium are neither reproducible nor constant, although the *E.M.F.* has approximately the same value as the constant cells. Saturated cells containing potassium sulphate are neither reproducible nor constant; the mercurous sulphate in them is distinctly hydrolysed, and the *E.M.F.* is markedly higher than that of the other cells. Saturated cells containing copper sulphate agree well among themselves, but are not constant. The *E.M.F.* is approximately one-third that obtained for the other cells, which indicates that the lead of the amalgam replaces the copper, and a copper amalgam is produced. Unsaturated cells containing the sulphates of sodium, zinc, nickel, cobalt, and manganese are just as reproducible as the saturated cells, they have the same *E.M.F.*, and are constant for a time, and then exhibit a decreasing *E.M.F.* Unsaturated cells containing the sulphates of lithium, magnesium, and cadmium have approximately the same *E.M.F.* as the saturated cells, and they

are equally unsatisfactory. Attempts to ascertain the cause of the unsatisfactory nature of these cells were without result.

J. F. S.

A New 0.1N-Calomel Electrode Design. A. E. KOEHLER (*J. Biol. Chem.*, 1920, **41**, 619—620).—This type of electrode was designed to overcome the changes in normality which the solutions in other patterns of instruments are apt to show. The apparatus is illustrated, and has been used for two months without showing any change in *E.M.F.*

J. C. D.

Platinised Glass Electrodes for Electrolytic Estimations. G. MEILLÈRE (*J. Pharm. Chim.*, 1920, [vii], **21**, 311—313).—Electrodes suitable for many purposes may be made by fusing a small piece of platinum wire into a glass tube, watch-glass, etc., then varnishing the glass with a solution of platinum chloride and an essential oil in methyl alcohol, and heating the glass until all organic matter has been oxidised. Several successive coatings may be applied in order to obtain a suitable layer of platinum on the glass. In some cases, it is advantageous to etch the glass with hydrofluoric acid before the platinum varnish is applied.

W. P. S.

Conduction of Electricity by Free Electrons and Carriers.
III. Migration Velocity of Particles moving under Forces in Viscous Media. P. LENARD, W. WEICK, and HANS FERD. MAYER (*Ann. Physik*, 1920, [iv], **61**, 665—741. Compare *ibid.*, 1900, 312).—A theoretical paper in which relationships are deduced for expressing and calculating the velocity of ions and other carriers of electricity in various media. Values are calculated for the radius (r) and the number of molecules of water (n) combined with the following ions in aqueous solution: H^+ , $n=1.4$, $r=0.9 \times 10^{-8}$ cm.; OH^+ , $n=2.5$, $r=1.4 \times 10^{-8}$ cm.; Li^+ , $n=19$, $r=5.0 \times 10^{-8}$ cm.; Na^+ , $n=12$, $r=4.2 \times 10^{-8}$ cm.; K^+ , $n=7$, $r=3.1 \times 10^{-8}$ cm.; Rb^+ , $n=6$, $r=2.9 \times 10^{-8}$ cm.; Cs^+ , $n=6$, $r=2.8 \times 10^{-8}$ cm.; F^+ , $n=11$, $r=3.9 \times 10^{-8}$ cm.; Cl^+ , $n=6$, $r=3.2 \times 10^{-8}$ cm.; Br^+ , $n=6$, $r=3.0 \times 10^{-8}$ cm.; I^+ , $n=6$, $r=2.9 \times 10^{-8}$ cm. It is shown that there is a distinct parallelism between the value of n and the temperature-coefficient of the migration velocity.

J. F. S.

Alternating Current Electrolysis. S. MARSH (*Proc. Roy. Soc.*, 1920, [A], **97**, 124—144).—Solutions of sulphuric acid and barium hydroxide have been electrolysed with alternating current of varying frequency by means of electrodes of gold, platinum, and nickel. In the case of platinum foil electrodes and sulphuric acid, the amount of evolution of gas decreases rapidly with time, and eventually no more gas is evolved. The amount evolved decreases with increasing frequency of the current; when thin platinum electrodes were used, the amount was less, but no simple relationship between the volume of gas evolved and the thickness

of the electrode was observed. The time-volume curves resemble the saturation curves obtained in radioactive measurements. With gold electrode and sulphuric acid, the rate of evolution of gas falls off rapidly with time, but for frequencies less than 48, gas is still given off at the electrodes for a much longer time than with platinum, and the total volumes of gas are considerably smaller than in the case of platinum. In the case of nickel, a copious evolution of hydrogen occurred for twenty minutes, beyond which the experiment could not be continued, owing to solution of the electrode. With barium hydroxide as electrolyte, the rate of evolution decreases with time and with increasing frequency, but the time-volume curves are practically straight lines. The volume of gas liberated is much greater than in acid solutions. Gold and platinum behave very similarly in barium hydroxide solution, but nickel only evolves the smallest quantity of hydrogen with a frequency of 60 cycles, and even with 40 cycles the volume of gas is too small to measure. Two suggestions are put forward to explain the phenomena: (i) the oxidation of the electrode, coupled with subsequent reduction by the hydrogen of the next half-period; (ii) the absorption and adsorption of hydrogen by the electrode, coupled with recombination with oxygen of the next half-period. These processes are not mutually exclusive, and it is possible that both agencies are operative in degrees varying with the metal employed.

J. F. S.

Electro-endosmosis and the Preparation of Solid Alkali-metal Amalgams. SUMNER B. FRANK and JAMES R. WITROW (*J. Amer. Chem. Soc.*, 1920, **42**, 671—675).—A number of experiments on electro-endosmosis show that it is modified by the type of porous cell used, but that an increased voltage and current density will always cause it to take place. Using solutions of potassium chloride, potassium sulphate, strontium chloride, and calcium acetate, endosmosis is always observed if the voltage is more than 8. The phenomenon is made very visible by the following experimental arrangement. The solution, saturated by preference, is placed in a beaker fitted with any form of platinum anode, and a porous cell is immersed to a depth of about 5—10 mm. in the solution, and about 50 grams of mercury, which serves as cathode, poured in. Contact is made with the mercury in the usual way, and a voltage of 20—25 is applied. In about sixty minutes, the solution will have entered and filled the porous pot to a height of about 3—4 cm. In these experiments, solid amalgams of potassium and strontium were obtained, but in the case of calcium, no amalgam was obtained, only a mixture of calcium hydroxide and finely divided mercury.

J. F. S.

Electrical Characteristics of Dye Colloids. RUDOLF KELLER (*Kolloid Zeitsch.*, 1920, **26**, 173—178. Compare A., 1919, ii, 491).—A continuation of the previous discussion (*loc. cit.*), in which the reason for the discrepancy between the author's experiments and the statements of many text-books is given. It is shown

that the statement of the text-books refers to dilute solutions of dyes where the substances in solution are ion disperse systems and the coloured cation naturally travels to the cathode, whereas the author's experiments were carried out with concentrated dye solutions which were colloid disperse systems and the cation wandered in the opposite direction.

J. F. S.

Influence of Molecular Constitution and Temperature on Magnetic Susceptibility. IV. Further Applications of the Molecular Field. A. E. OXLEY (*Phil. Trans.*, 1920, [A], 220, 247—289. Compare A., 1914, ii, 424; 1915, ii, 219).—A theoretical paper in which the discussion previously published is continued. The applications of local molecular force, in diamagnetic, paramagnetic, and ferromagnetic media, have been extended to interpret the ultimate strength of crystalline and vitreous media. It is to be expected, since the permanent set which occurs prior to breaking is due to slipping along the cleavage planes within the crystal grains, that the material will be fractured when the applied mechanical stress is equal to that produced internally by the local molecular force. The internal stress within the material is of the order 2×10^9 dynes per sq. cm., which is approximately the mean of the ultimate strengths of crystalline and vitreous media. As a consequence of this internal stress, the energy per unit volume will be 2×10^9 ergs, and this energy is a measure of the latent heat of fusion per c.c. It is found that the elastic constants of a variety of ferromagnetic, diamagnetic, and paramagnetic media are of the same order, several diamagnetic and paramagnetic media even surpassing steel in their power to resist distortion. The energy change which occurs on crystallisation is compatible with a volume change of the same order of magnitude as that accompanying crystallisation, and the change of volume on crystallisation may therefore be interpreted as a magneto-striction effect of the local molecular force. The magneto-striction effect depends on molecular orientation, which is proportional to the square of the magnetic force. A physical interpretation has been given of the large values of the coefficients N and a' of the molecular fields in ferromagnetic and diamagnetic crystalline media respectively. These coefficients are the reciprocals of the limiting local susceptibilities of the media under field strengths equal to the respective molecular fields. The local susceptibility of a diamagnetic molecule is comparable with that of a ferromagnetic molecule, and the two vary in the same way with field strength and temperature. In diamagnetic media, however, magnetic hysteresis will be inappreciable, since the molecule as a whole possesses a zero magnetic moment. Mechanical hysteresis in diamagnetic media will be of the same order as in ferromagnetic media. It has been previously shown (*loc. cit.*) that the magneton may be a constituent of the diamagnetic hydrogen molecule. This idea may be extended to carbon and the hydrocarbons in general, where the molecular susceptibility can be directly calculated from the atomic susceptibilities of the component

of the electrode was observed. The time-volume curves resemble the saturation curves obtained in radioactive measurements. With gold electrode and sulphuric acid, the rate of evolution of gas falls off rapidly with time, but for frequencies less than 48, gas is still given off at the electrodes for a much longer time than with platinum, and the total volumes of gas are considerably smaller than in the case of platinum. In the case of nickel, a copious evolution of hydrogen occurred for twenty minutes, beyond which the experiment could not be continued, owing to solution of the electrode. With barium hydroxide as electrolyte, the rate of evolution decreases with time and with increasing frequency, but the time-volume curves are practically straight lines. The volume of gas liberated is much greater than in acid solutions. Gold and platinum behave very similarly in barium hydroxide solution, but nickel only evolves the smallest quantity of hydrogen with a frequency of 60 cycles, and even with 40 cycles the volume of gas is too small to measure. Two suggestions are put forward to explain the phenomena: (i) the oxidation of the electrode, coupled with subsequent reduction by the hydrogen of the next half-period; (ii) the absorption and adsorption of hydrogen by the electrode, coupled with recombination with oxygen of the next half-period. These processes are not mutually exclusive, and it is possible that both agencies are operative in degrees varying with the metal employed.

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that the statement of the text-books refers to dilute solutions of dyes where the substances in solution are ion disperse systems and the coloured cation naturally travels to the cathode, whereas the author's experiments were carried out with concentrated dye solutions which were colloid disperse systems and the cation wandered in the opposite direction.

J. F. S.

Influence of Molecular Constitution and Temperature on Magnetic Susceptibility. IV. Further Applications of the Molecular Field. A. E. OXLEY (*Phil. Trans.*, 1920, [A], 220, 247—289. Compare A., 1914, ii, 424; 1915, ii, 219).—A theoretical paper in which the discussion previously published is continued. The applications of local molecular force, in diamagnetic, paramagnetic, and ferromagnetic media, have been extended to interpret the ultimate strength of crystalline and vitreous media. It is to be expected, since the permanent set which occurs prior to breaking is due to slipping along the cleavage planes within the crystal grains, that the material will be fractured when the applied mechanical stress is equal to that produced internally by the local molecular force. The internal stress within the material is of the order 2×10^9 dynes per sq. cm., which is approximately the mean of the ultimate strengths of crystalline and vitreous media. As a consequence of this internal stress, the energy per unit volume will be 2×10^9 ergs, and this energy is a measure of the latent heat of fusion per c.c. It is found that the elastic constants of a variety of ferromagnetic, diamagnetic, and paramagnetic media are of the same order, several diamagnetic and paramagnetic media even surpassing steel in their power to resist distortion. The energy change which occurs on crystallisation is compatible with a volume change of the same order of magnitude as that accompanying crystallisation, and the change of volume on crystallisation may therefore be interpreted as a magneto-striction effect of the local molecular force. The magneto-striction effect depends on molecular orientation, which is proportional to the square of the magnetic force. A physical interpretation has been given of the large values of the coefficients N and a' of the molecular fields in ferromagnetic and diamagnetic crystalline media respectively. These coefficients are the reciprocals of the limiting local susceptibilities of the media under field strengths equal to the respective molecular fields. The local susceptibility of a diamagnetic molecule is comparable with that of a ferromagnetic molecule, and the two vary in the same way with field strength and temperature. In diamagnetic media, however, magnetic hysteresis will be inappreciable, since the molecule as a whole possesses a zero magnetic moment. Mechanical hysteresis in diamagnetic media will be of the same order as in ferromagnetic media. It has been previously shown (*loc. cit.*) that the magneton may be a constituent of the diamagnetic hydrogen molecule. This idea may be extended to carbon and the hydrocarbons in general, where the molecular susceptibility can be directly calculated from the atomic susceptibilities of the component

atoms. The results in other cases are unconvincing, but the fact that departures from the additive law occur in these cases leads to the conclusion that some disturbing influence has been overlooked.

J. F. S.

Magnetic Properties of Nickel-Copper Alloys. R. GANS and A. FONSECA (*Ann. Physik*, 1920, [iv], **61**, 742—752).—The magnetic susceptibility of nickel-copper alloys has been measured over a range of concentrations from 20.3% nickel to 60.2% nickel at temperatures from -230° to 55° , and the transformation point determined for each concentration. A series of susceptibility measurements are also given for 15° for the whole of the alloys. The results show that the Tammann rule (A., 1909, ii, 16) is not true in the present case, and that ferromagnetic substances dissolved in non-magnetic crystals yield ferromagnetic alloys. Copper-nickel alloys form a complete series of mixed crystals except over the range 45—50% nickel, in which nickel crystals saturated with copper and copper crystals saturated with nickel exist. The present results are analogous to those obtained for cobalt-copper alloys, except that in this case the gap in the mixed crystal series is considerably larger.

J. F. S.

Magnetic Susceptibility of Antimony and Bismuth: Form of the Magnetron. HECTOR ISNARDI and RICHARD GANS (*Ann. Physik*, 1920, [iv], **61**, 585—590).—The specific susceptibility of bismuth and antimony has been determined by the Weiss method, using fields lying between $H=1029$ Gauss and $H=13680$ Gauss. The results show that the magnetic susceptibility of these metals is independent of the strength of the field, and that the apparent dependence found by Honda and Owen (A., 1910, ii, 686; 1912, ii, 425) is probably due to the presence of iron as an impurity in the material and also to errors of measurement. The following mean values are found: bismuth, $-\chi \cdot 10^{-6} = 1.346$; antimony, $-\chi \cdot 10^{-6} = 0.8138$. From the Gans theory it is shown that the principal moments of inertia of the magnetron are identical. This result is obtained only for bismuth and antimony, but judging from the measurements of Honda and Owen it is probably true for other elements.

J. F. S.

Specific Heat of Carbon Dioxide and Steam. W. T. DAVID (*Phil. Mag.*, 1920, [vi], **39**, 551—553).—A theoretical paper in which the author advances the suggestion that the specific heat of steam and carbon dioxide depends not only on the temperature, but also on volume and density. At any particular temperature the greater the volume of the gas the greater its specific heat, and the greater the density the less its specific heat. In a previous communication (A., 1911, ii, 1046) the author has shown that carbon dioxide and steam emit radiation in appreciable quantity in the neighbourhood of 1000° and very strongly in the neighbourhood of 2000° . Consequently, the specific heat of these gases may be

expected to vary slightly with volume and density at 1000° and very markedly at 2000°.

J. F. S.

Secondary Valencies and Fusibility. ARRIGO MAZZUCCHELLI (*Gazzetta*, 1920, 50, i, 93—97).—According to Nernst ("Kinetische Theorie der Materie," Leipzig, 1913), the varying fusibilities of the elements are explainable by their different numbers of primary and secondary valencies, the reciprocal attractions of which keep the atoms fixed in the crystalline network characteristic of the solid state. The author extends this conception to the interpretation of certain apparently contradictory regularities in the fusibility of metallic and non-metallic compounds.

With the latter the fusibility diminishes as the number of atoms in the molecule increases, the more complicated molecules appearing to find greater difficulty in assuming the condition of irregular movement characteristic of liquids; the same rule holds for the volatility, a measure of which is afforded by the critical temperature. The correlation between molecular complexity and melting or boiling point is most marked in homologous series of carbon compounds, and is, indeed, so general for non-metallic compounds that divergences are utilised as criteria of polymerisation in the liquid state.

With compounds of the metals, on the other hand, fusibility and volatility increase with increase in the complexity of the molecule.

To explain the different behaviour of non-metallic and metallic compounds the author advances the following considerations. From Nernst's assumption that the heavy metals are relatively infusible because their numerous primary and secondary valencies hold the atoms firmly in the crystalline network, the conclusion is drawn that combination of the metallic atom with an increasing number of oxygen or other non-metal atoms results in increasing saturation of the valencies in the interior of the molecule. Thus, the number of valencies available to maintain the molecules united in the crystalline aggregate is diminished and the fusibility consequently increased. In other words, entry of oxygen, chlorine, etc., introduces into the molecule that internal saturation of the valencies to which oxygen, chlorine, etc., owe their fusibility. This explanation applies, not only to binary compounds, but also to those of higher orders and to hydrated salts. Further, it is not invalidated by the information furnished in recent years by X-ray diffraction spectra, which show that the various atoms are distributed almost uniformly in the crystalline network.

T. H. P.

Apparatus for the Determination of Melting Points.

L. M. DENNIS (*J. Ind. Eng. Chem.*, 1920, 12, 366—368).—The apparatus is similar to that described by Thiele (A., 1907, ii, 330), but the lower portion is inclined downwards; the "rising" portion of the loop is of narrower diameter, and enters the main tube at an angle. It is claimed that there is better circulation of the sulphuric acid and a more uniform temperature can be maintained.

W. P. S.

Fractionation Flask for the Distillation of Frothing Liquids. EMIL LENK (*Chem. Zeit.*, 1920, **44**, 330).—The lower end of a condenser is fused on to the neck of an ordinary fractionating flask at a point below the outlet tube of the latter, and is then bent upwards to form a reflux condenser. These two outlets from the flask are connected with a pump, the communication being controlled by a three-way tap, so that a vacuum can be produced in either direction. In distilling a viscous liquid the reflux condenser is first exhausted, and the froth will then rise into it and the liquid subsequently fall back into the flask. When the liquid in the flask is boiling steadily a vacuum is created in the other direction and the distillation continued. To facilitate the return of substances solid at the ordinary temperature from the reflux condenser, hot water may be circulated through the cooling jacket. The inner tube of the condenser is constricted at intervals to form a series of pear-shaped bulbs. C. A. M.

A Simple Distillation Apparatus for Separation of Water. GEO. W. WALKER (*Chem. News*, 1920, **120**, 222).—In distilling solvents such as benzene and chloroform, which contain water, a distilling flask with two necks is used. One neck is connected by rubber tubing with a condenser, the other by rubber tubing with a flask cooled in water. At the commencement of the distillation, the tube leading to the condenser is closed by a clip, and the water allowed to distil off into the flask. The first clip is then opened, and the tube leading to the flask closed by a second clip. Distillation of the solvent then proceeds. J. R. P.

The Energy of the Atomic Linkings in Diamond and in Aliphatic Hydrocarbons. K. FAJANS (*Ber.*, 1920, **53**, [B], 643—665).—The heat of combustion of a saturated aliphatic hydrocarbon may be regarded as the result of the heat of formation of a carbon hydrogen bond (x), that of a simple C-C linking in compounds (y) [the similar linking in diamond being denoted by y'], the heat of formation of liquid water from 1 gram atom of atomic hydrogen and molecular oxygen (v), and the heat of formation of gaseous carbon dioxide from 1 gram atom of atomic carbon (monatomic carbon vapour) and molecular oxygen (z). For the special cases of propane and ethane the expressions may be written: $-8x + 8v - 2y + 3z = 526.7$ and $-6x + 6v - y + 2z = 370.9$, by subtraction of which there is obtained $-2x + 2v - y + z = 155.8$ Cal. as the expression of the increase in the heat of combustion due to the addition of the methylene group. Since z and v are independent of the substance under investigation, it follows that the magnitude $y + 2x$ is subject to but little variation, which is most simply explained by the hypothesis that x and y are constant to a first approximation, that is, the energy of a simple C-C or of a C-H linking is practically the same in different saturated aliphatic hydrocarbons. Further, an examination of the available data for various hydrocarbons leads to the conclusion that the energy of the

C-C linking in hydrocarbons is practically uninfluenced by the further attachment of the C atoms to other C or H atoms. If x and v are eliminated from the first two equations, the expression $z-2y=96.5$ Cal. is obtained; the number is rather considerably influenced by slight experimental errors in the data on which it is based, but a consideration of a large number of suitable estimations leads to the equation $z-2y=98\pm 8$. The recent work of Langmuir, Isnardi (A., 1915, ii, 738) and Franck, Knipping, and Krüger (this vol., ii, 145) allows v to be evaluated at 74.4 ± 2.8 Cal. Now the heat of combustion of the diamond is the result of two factors (a) the heat required to convert solid diamond into monatomic carbon vapour [heat of sublimation], and (b) the heat of combustion of the vapour (z) to carbon dioxide. Using Roth's values, one obtains $z-2y'=94.4$ Cal. Since, however, $z-2y=98\pm 8$, it follows that $y'-y=2\pm 4$ Cal., from which it is deduced that the heat of formation of a C-C linking in saturated hydrocarbons is practically the same as that in diamond. Since v is known, y is practically equal to y' , and $2y'$ represents the difference in energy between solid diamond and monatomic carbon vapour, the problem of dissecting the heat of formation of hydrocarbons resolves itself into the estimation of the heat of sublimation of diamond. This has been estimated by Fajans (*Zeitsch. Physik*, 1920, 1, 101) to be 287 Cal. The following values can thus be deduced: $z=351$ Cal., $y=137.5$ Cal., $v=74.4$, and $x=117$ Cal. The data are applied to the calculation of the heats of formation of a series of hydrocarbons, both from diamond and hydrogen and from the atomic substances; in the latter case large positive values are always indicated, and it is interesting to note that the formation of the C-C and C-C linkings is associated with the development of 252 and 365 Cal. respectively, whereas the production of the C-C bond only evolves 136 Cal. Strictly speaking, it should be observed that the values assigned to the energy of the various linkings are only valid when all other available valencies of the carbon atoms are saturated.

Similar considerations are applied to the combustion of carbon in oxygen. The relatively smaller development of energy which is associated with the first stage of the oxidation is only apparent; when the heat of sublimation of diamond is taken into account, the equation may be written $C_{\text{vapour}} + \frac{1}{2}O_2 = CO + 314$ Cal., whilst $CO + \frac{1}{2}O_2 = CO_2 + 67.8$ Cal.

The paper concludes with a criticism of the recent communications of von Weinberg (A., 1919, i, 314) and Padoa (A., 1919, ii, 97), for details of which the original must be consulted.

H. W.

The Energy of Atomic Linking in Graphite and in the Aromatic Hydrocarbons. A. L. VON STEIGER (*Ber.*, 1920, 53, [B], 666—680 Compare Fajans, preceding abstract).—The investigation was undertaken with the object of referring the unique position of aromatic ring systems in organic chemistry to

the peculiar nature of their carbon atoms. It has been shown by Debye and Scherrer (A., 1917, ii, 437) from a consideration of the crystalline structure of graphite that the carbon atoms in the latter may be regarded as tervalent if the energy of the fourth bond is neglected on account of its smaller order of magnitude. Proceeding in the same manner as Fajans (*loc. cit.*), the author finds that, for purposes of calculation, the carbon atoms of purely aromatic hydrocarbons which are made up of simple or condensed six-carbon rings may be regarded as tervalent, and that all C-C linkings are equivalent. It is further found that the energy of the C-C linking in graphite is very nearly the same as in aromatic hydrocarbons. Since the molar heat of sublimation of graphite has been calculated (Fajans, *Zeitsch. Physik*, 1920, **1**, 107), it is therefore possible to calculate the heat of combustion of an aromatic hydrocarbon, the constitution of which is known. It is interesting to note that the energy of the C-C and C-H groups in aromatic is greater than in aliphatic hydrocarbons, the respective values being 187.3 and 137.5 for the former and 137.7 and 117 Cal. for the latter.

Basing his ideas on the equality of energy of the C-C linking in graphite and in the purely aromatic hydrocarbons, the author traces a close analogy between the six-membered rings of the carbon planes in the former and the six-ring system of the latter, and is thus led to the following conception of the constitution of aromatic ring systems. The latter are composed of carbon atoms, which have the same disposition of valencies as the carbon atoms in graphite. The distance from one another is approximately 1.45×10^{-8} cm. The chief valencies lie in a plane and make an angle of 120° with one another. The existence of free subsidiary valencies of a smaller order of magnitude in the aromatic ring is very probable, and, if the analogy with graphite may be pushed so far, they must be considered as placed at right angles to the plane of the six-carbon ring.

H. W.

Pressure and Temperature-coefficients, Volume, and Heat Effects in Bivariant Systems. P. H. J. HOENEN (*Proc. K. Akad. Wetensch. Amsterdam*, 1920, **22**, 526—530).—A mathematical paper in which equations are developed by which the composition may be calculated of each phase of a system having n components in which there may be n co-existing phases and in which p and T are independent variables. Further equations are developed for calculating the relation between the pressure- and temperature-coefficients for the transition of the components from one phase to another in a system of n components and l phases when $n \geq l$; further expressions give the heat effects and the volume changes which accompany the transition.

J. F. S.

Van der Waals's Force of Cohesion. P. DEBYE (*Physikal. Zeitsch.*, 1920, **21**, 178—187).—A theoretical paper in which, from a consideration of electrical attraction of two molecules for one another, expressions are derived whereby the van der Waals's constant b may be calculated. Further expressions are developed

whereby the surface tension and the Eötvös constant may be calculated. J. F. S.

The Falling Sphere Viscosimeter. WILLIAM HOWIESON GIBSON and LAURA MARY JACOBS (T., 1920, 117, 473—478).

Orientation of Molecules in Surfaces, Surface Energy, Adsorption, and Surface Catalysis. V. Adhesionial Work between Organic Liquids and Water. WILLIAM D. HARKINS, GEORGE L. CLARK, and LATHROP E. ROBERTS (*J. Amer. Chem. Soc.*, 1920, 42, 700—712. Compare A., 1917, ii, 238, 239; 1916, ii, 222, 223).—A table is given which contains the free surface energy, the adhesionial work per sq. cm., the interfacial free energy, the surface adhesion, and the densities of about seventy organic liquids. Of these liquids about thirty-four have been freshly investigated. The data presented are in keeping with the view that the molecules at interfaces are oriented. It is assumed from the formulæ that carbon disulphide has a symmetrical molecule and ethyl mercaptan an unsymmetrical molecule. The cohesive work is much greater in the former case than in the latter, 62.8 ergs per sq. cm. instead of 43.6, whilst the adhesionial work between water and carbon disulphide is much less (55.8 ergs per sq. cm.) than it is between water and mercaptan (68.5 ergs per sq. cm.). These facts are readily explained by the orientation theory. Thus the attraction between octane and water is relatively small, the adhesionial work being only 43.76 ergs. The octane molecule contains 26 atoms, and yet the introduction of one oxygen atom at the end of the chain more than doubles the adhesionial work, and increases it to 91.77 ergs. A similar introduction of one oxygen atom into isopentane increases the adhesionial work towards water from 36.9 to 92.5, an increase of 150%. The substitution of an amine group for a hydrogen atom at the end of a chain causes a similar increase, as also does the substitution of $-\text{COOH}$, $-\text{CN}$, $-\text{CO}$, or any similar groups. The great magnitude of the effect, when it is considered that the addition of 1 atom to 26 causes an increase of 132%, is strong evidence that the oxygen is turned towards the water. It is found that in only three cases out of fifty-eight is the cohesive work of an organic liquid greater than its adhesionial work toward water. The three substances are carbon disulphide, ethylene dibromide, and acetylene tetrabromide. The excess of the adhesionial over the cohesive work increases as the symmetry of the molecule decreases. This is also strong evidence in favour of the orientation theory. The benzene hydrocarbons are more polar than the paraffin hydrocarbons. Aniline is found to be extremely polar in comparison with most of the organic liquids. The polar characteristics of the benzene derivatives are distributed much more over the whole molecule than is the case with the paraffin derivatives. The total surface energy and the free surface energy are not due to the orientation of the molecules, but to the stray surface field, and this is decreased by the orientation. J. F. S.

Adsorption and Solubility. E. F. LUNDELIUS (*Kolloid Zeitsch.*, 1920, **26**, 145—151).—The adsorption of iodine from solutions in carbon tetrachloride, carbon disulphide, and chloroform by blood charcoal has been determined at 19—20°. The results are plotted as absorption isotherms for the surface of 1 gram of charcoal. In general, the results show that the adsorption is inversely proportional to the solubility. The adsorption of vapours of toluene, carbon disulphide, carbon tetrachloride, chloroform, benzene, and hexane by blood charcoal has also been determined, and it is shown that approximately equal volumes of the various substances are adsorbed from their saturated vapours, from which it follows that the thickness of the layer of adsorbed material is the same in all cases examined.

J. F. S.

Relationship between the Height of Capillary Rise, the Time, and the Concentration in the Capillary Rise in Filter Paper. HANS SCHMIDT (*Kolloid Zeitsch.*, 1920, **26**, 152—159, Compare A., 1913, ii, 721; 1919, ii, 185).—The height to which solutions of glycerol and dextrose of various concentrations rise in filter paper has been determined at temperatures 15—17°. Also the rate of rise has been ascertained in all cases. The results show that the constant of the velocity of capillary rise is inversely proportional to the viscosity of the solution. It is also shown that it is possible, from the relationship between the time required by a given solution to rise to a definite height and that of pure water, to calculate approximately the concentration of the solution.

J. F. S.

Cause of the Influence of Ions on the Rate of Diffusion of Water through Collodion Membranes. I. JACQUES LOEB (*J. Gen. Physiol.*, 1920, **2**, 387—408).—In this paper it is shown that in electrical endosmosis through a collodion membrane the influence of electrolytes on the rate of transport of liquids is the same as in free osmosis. Since the influence of electrolytes on the rate of transport in electrical endosmosis must be ascribed to their influence on the quantity of electrical charge on the unit area of the membrane, it follows that the same explanation holds for the influence of electrolytes on the rate of transport of water into a solution through a collodion membrane in the case of free osmosis. It may, therefore, be concluded that when water is separated from a solution of an electrolyte by a collodion membrane, the rate of diffusion of water by free osmosis is accelerated by the ion with the opposite sign of charge to that of the watery phase of the double layer, and that it is retarded by ions with like charge. The influence of the ions of an electrolyte in raising or lowering the charge on the unit area of the solution side of the membrane, compared with that on the water side, will determine whether osmosis is positive or negative. A further conclusion is that in lower concentrations of many electrolytes the density of electrification of the double layer increases with an increase in concentration, whilst in

higher concentrations of the same electrolytes it decreases with an increase in concentration. In the case of a number of electrolytes the turning point lies about $M/512$ or $M/256$.

J. C. D.

Extension of Braun's Law. P. H. J. HOENEN (*Proc. K. Akad. Wetensch. Amsterdam*, 1920, **22**, 531–535).—A mathematical paper in which it is shown that Braun's law, which has the form $(\partial x/\partial p)_T: (\partial x/\partial T)_p = T\Delta V/Q$, is a particular case of a more general law which is developed in the present work. The general law is formulated thus:

$$(\partial x/\partial p)_T \cdot Qx/T + (\partial x/\partial T)_p \cdot \Delta V_x + (\partial y/\partial p)_T \cdot Qy/T + (\partial y/\partial T)_p \cdot \Delta V_y + \text{etc.} = 0,$$

in which $(\partial x/\partial p)_T$ and $(\partial y/\partial p)_T$ are the pressure-coefficients of the solubility of x and y respectively, $(\partial x/\partial T)_p$ and $(\partial y/\partial T)_p$ are the temperature-coefficients, ΔV_x and ΔV_y the differential increase in volume due to x and y respectively.

J. F. S.

Determination of the Dissociation Constants of some Mineral Acids. EMILE BLANC (*J. Chim. Phys.*, 1920, **18**, 28–45).—The degree of dissociation of a number of acids and the degree of hydrolysis of the sodium salts of some of them have been determined by means of conductivity, potential, and the indicator methods. The following values for the degree of hydrolysis are found at 25° for the salts named: sodium phosphate 0.012*N* is hydrolysed 34.1%; disodium hydrogen phosphate, 0.012*N*, 0.066%; sodium phosphite, 0.0075*N*, 0.021%; sodium dihydrogen arsenite, 0.0104*N*, 0.394%; sodium arsenate, 0.002*N*, 8.0%; disodium hydrogen arsenate, 0.002*N*, 0.0455%; sodium selenite, 0.0108*N*, 0.379%; sodium hydrogen tellurite 0.0075*N*, 0.0022%; sodium tellurite, 0.0075*N*, 0.773%; sodium hydrogen tellurate, 0.0093*N*, 0.117%; sodium tellurate, 0.0093*N*, 13.97%; potassium molybdate, 0.00975*N*, 0.359%; and potassium tungstate, 0.0162*N*, 0.011%. The following new dissociation constants have been calculated from the experimental results: phosphorous acid, $K_2 = 2 \times 10^{-5}$; arsenic acid, $K_2 = 4 \times 10^{-5}$; $K_3 = 6 \times 10^{-10}$; selenious acid, $K_1 = 2 \times 10^{-3}$, $K_2 = 5 \times 10^{-8}$; tellurous acid, $K_1 = 2 \times 10^{-3}$, $K_2 = 1 \times 10^{-8}$; telluric acid, $K_1 = 6 \times 10^{-7}$, $K_2 = 4 \times 10^{-11}$.

J. F. S.

A Model for Demonstrating Crystal Structure. HERBERT P. WHITLOCK (*Amer. J. Sci.*, 1920, [iv], **49**, 259–264).—The model, which is used for demonstrating the spatial distribution of the atoms in a crystal as revealed by the X-ray method of Bragg, consists of a number of thin glass rods mounted vertically in a double diaphragm perforated with holes arranged in a symmetrical pattern, a centred square pattern, for instance, for cubic, tetragonal, and orthorhombic crystals, or an equilateral triangular pattern for hexagonal and rhombohedral crystals. The atoms are represented by spherical wooden beads bored with a hole to fit the rods. The beads are spaced accurately on the rods to represent different groupings of atoms, and are fastened in position by a drop of glue.

Beads of different colours are used to represent different kinds of atom.

E. H. R.

Differentiation between Molecular and Colloidal Solutions. WA. OSTWALD (*Kolloid Zeitsch.*, 1920, **26**, 138—140).—It is suggested that molecular and colloidal solutions may be differentiated by an examination of the ice produced by freezing them. In the colloidal solutions it is suggested that a difference in composition of successive horizontal layers may be found, due to the settling of the colloidal particles during the freezing.

J. F. S.

Automatic Sedimentation Recorder and its Use in some Colloid-chemical Problems. SVEN ODÉN (*Kolloid Zeitsch.*, 1920, **26**, 100—121).—An apparatus is described whereby the rate of sedimentation of a suspension may be automatically recorded. The apparatus consists of a thin gold-plated disk, which is suspended to one arm of a sensitive balance and hangs inside a cylinder of nearly the same diameter in which the suspension is placed. The precipitation plate is exactly balanced by weights on the other pan, and when a small quantity of the suspended matter falls on it, it sinks; this operates an electric contact, which by means of relays causes a small iron pellet to be thrown on the weight pan. The precipitation plate is thus raised, and the contact broken. Each time the two pans are of exactly the same weight a mark is made on a slowly rotating paper coil which marks the time. Thus the weight and time, and consequently the rate of sedimentation, are known. This apparatus has been used in determining the mean and actual diameter of suspensoid particles in the case of silver bromide, the aggregation time, and the dependence of the aggregation time on the concentration of the particles and the electrolyte concentration.

J. F. S.

Coagulating Power of some Electrolytes. (MLLE.) N. BACH (*J. Chim. Phys.*, 1920, **18**, 46—64).—The relative coagulating power of ions of the alkali metals and the halogens has been determined by means of a new method, which consists in measuring the opacity number of the electrolyte. The opacity number is the number of c.c. of a normal solution of the electrolyte which will produce a definite turbidity in a colloidal solution. This quantity can be determined with great precision, and consequently the method is well suited to this purpose. The coagulating power of an electrolyte is the reciprocal of the opacity number. It is shown that the ratio of the opacity numbers of two electrolytes depends only on the nature of the colloid, and it may be that it is even independent of this. The opacity numbers are all referred to that of potassium chloride as unity. It is found that the coagulating power of the alkali ions follows the order: $\text{Cs}' > \text{Rb}' > \text{NH}_4' > \text{K}' > \text{Na}' > \text{Li}'$ and the halogen ions $\text{Cl}' > \text{Br}' > \text{I}'$. Other things being equal, an alkali ion coagulates a negative colloid more powerfully and protects a positive colloid more effectually the more electropositive it is, and a halogen ion coagulates a positive colloid and

protects a negative colloid more strongly the more electronegative it is. The coagulating power is always much more marked than the protecting power. In the case of the halogen ions the difference between the discharge potentials is proportional to the difference between the coagulating power. The coagulating power of potassium chloride mixed with hydrochloric acid, potassium hydroxide, barium chloride, potassium sulphate, lanthanum chloride, sodium citrate, and potassium ferrocyanide has also been measured, and it is shown that both the coagulating power and the protecting power are additive. It is also shown that colloidal solutions are extremely sensitive to traces of multivalent impurities. J. F. S.

Direct Experimental Determination of the Concentration of Potassium and Sodium Ions in Soap Solutions and Gels. CYRIL SEBASTIAN SALMON (T., 1920, 117, 530—542).

Emulsions. I. A New Method of Determining the Inversion of Phases. SHANTI SWARUPA BHATNAGAR (T., 1920, 117, 542—552).

Non-, Uni-, and Bi-variant Equilibria. XX. F. A. H. SCHREINEMAKERS (*Proc. K. Akad. Wetensch. Amsterdam*, 1920, 22, 542—554. Compare A., 1917, ii, 454; this vol., ii, 169).—A further theoretical paper dealing with the conditions of equilibrium in non-variant, uni-variant, and bi-variant systems. The present paper deals with the equilibria of n components in n phases, in which the quantity of one of the components approaches the zero value, and the influence of a new substance on a non-variant (P or T) equilibrium. J. F. S.

Equilibrium Conditions of the Reaction between Silver Sulphide and Hydrogen. F. G. KEYES and W. A. FELSING (*J. Amer. Chem. Soc.*, 1920, 42, 246—251).—The equilibrium $\text{Ag}_2\text{S} + \text{H}_2 \rightleftharpoons 2\text{Ag} + \text{H}_2\text{S}$ has been investigated at the temperatures 750° , 811° , and 890° absolute, by the method and with the apparatus previously described by Keyes (A., 1912, ii, 627). The following values of the equilibrium constant were obtained: 749.15° , $K=0.359$; 811.25° , $K=0.325$; and 889.63° , $K=0.278$. From the results it is shown that the heat of the reaction is to be expressed $\text{Ag}_2\text{S} + \text{H}_2 = 2\text{Ag} + \text{H}_2\text{S} + 2410$ cal. The equilibrium constant, between 750° and 890° absolute, is expressed as a function of the temperature by means of the expression $\log_{10} K = 525.8/T - 1.1470$. The corresponding expression for the decrease in free energy over the same temperature range is $-\Delta F = RT \log_e K = 2408 - 5.253T$. J. F. S.

Heterogeneous Equilibria between Aqueous and Metallic Solutions. Interaction of Mixed Salt Solutions and Liquid Amalgams. VI. Ionisation Relations of Sodium and Potassium Chlorides, Bromides, and Iodides in Mixtures. L. S. WELLS and G. MCP. SMITH (*J. Amer. Chem. Soc.*, 1920, 42, 185—205. Compare A., 1918, ii, 67; 1917, ii, 455).—The equilibrium between sodium and potassium amalgams and

mixtures of sodium and potassium chloride, bromide, and iodide respectively, has been investigated. It is shown that at a fixed total salt concentration the value of the equilibrium constant $C_e = nk = (K_{H_2O})(NaX)/(Na_{H_2O})(KX)$ decreases with increasing concentration of the amalgam. At fixed amalgam and total salt concentrations, but with varying salt ratio, the value of C_e is constant. At a fixed amalgam concentration the value of C_e decreases with the increasing concentration of the mixed (equivalent) salt solution. Ion-fraction calculations are put forward for aqueous binary salt mixtures containing the salts in equivalent proportions. It is found that the simple potassium-ion fraction decreases, whilst the sodium-ion fraction correspondingly increases with the increasing total salt concentration. These changes take place the more rapidly the higher the average atomic weight of the halogens in the mixture. These results are not in keeping with the view that at equivalent concentration salts of the same type are ionised to the same extent. The general results of the work are readily explained in terms of Werner's theory concerning the formation and dissociation of higher order compounds. J. F. S.

Rate of Corrosion of Aluminium. GEORGE HERBERT BAILEY (*J. Soc. Chem. Ind.*, 1920, **39**, 118—120r).—A measure of the extent to which a sample of aluminium is corroded, in terms of the metal so corroded per day per 100 sq. cm. of surface, is given by $CR = 9/8(S + w - W)$, where W is the weight of the sheet employed, w its weight after exposure, and S the weight of the precipitate obtained after ignition. The variation of CR with the concentration of the corrosive solution employed at 12° is shown by a number of curves in which $\log CR$ is plotted against concentration. In the case of sodium, potassium, and barium hydroxides the curves are straight lines showing increasing attack as the concentration increases, whereas the ammonia curve rises to a maximum and then falls off. For the mineral acids, CR is fairly steady up to $0.30N$; in the case of hydrochloric acid the curve then rises very steeply, whilst the curves for nitric and sulphuric acids rise more gradually to maximum values and then fall. At ordinary temperatures corrosion ceases, for example, in the case of sodium hydroxide or hydrochloric acid, when the solution has become exhausted, but at higher temperatures, in the neighbourhood of 100° , attack continues indefinitely, with formation, in the case of hydrochloric acid, of colloidal basic salts. The formation of a protective coating causes the rate of attack to fall off considerably with time, more rapidly in the case of impure metal than with purer specimens. The protective film, in the case of ammonia, is only about 0.01 mm. in thickness, but it has considerable insulating power for high-tension electric currents. E. H. R.

The Reversible Reaction between Iron and Steam. E. SCHREINER and F. B. GRIMNES (*Zeitsch. anorg. Chem.*, 1920, **110**, 311—334).—Measurements of the equilibrium pressures of water-vapour and hydrogen in the reaction $Fe + H_2O \rightleftharpoons FeO + H_2$ were

made between 595° and 920° , using an apparatus similar to that first employed by Deville (*Compt. rend.*, 1870, **70**, 1105, 1205). It was shown that refinements in the apparatus introduced by other workers with the object of accelerating the diffusion of the gases in the reaction tube were unnecessary. The values obtained for $K = p_{H_2O}/p_H$ were in good agreement, starting from either side of the equilibrium position. There are considerable discrepancies between the results obtained by different workers, particularly at high temperatures, where, in all cases, the value of K is much lower than that calculated from thermodynamic principles. The discrepancies are probably due to reactions in the solid phase, for example, the formation of solid solutions between iron and ferrous oxide, or to the different behaviour of different modifications of iron. Further experiments are suggested to test this hypothesis.

E. H. R.

The Influence of the Solvent on the Velocity of Reaction between certain Alkyl Iodides and Sodium β -Naphthoxide.
HENRY EDWARD COX (*T.*, 1920, **117**, 493—510).

Hydration as an Explanation of the Neutral Salt Effect.
ARTHUR JOHN WILSON (*J. Amer. Chem. Soc.*, 1920, **42**, 715—720).—The addition of 120 grams of sodium chloride to chrome tanning liquor (17 grams of Cr_2O_3 as sulphate per litre) increases the hydrogen-ion concentration about 50% and prevents the liquor from tanning skins. Other experiments show that the amount of 0.1*N*-sodium hydroxide necessary to produce a precipitate of basic chromic salts increases if certain neutral salts are added to the liquor, thus: 10 c.c. of the untreated liquor required 3.7 c.c., but the addition of 0.04 gram of sodium chloride increased the amount to 6.8 c.c. Using many salts the order of increase in the amount of sodium hydroxide required increases with the salts, potassium chloride (4.0 c.c.) < ammonium chloride < sodium chloride < magnesium chloride < magnesium sulphate < sodium sulphate < ammonium sulphate (11.6 c.c.). The author attributes this action to the hydration of the added salt with consequent increase of the acid concentration, and he calculates the number of molecules of water combined with one molecule of the salt in the case of sodium chloride for a number of dilutions; the following values are given: 4*N*, 10.9; 3*N*, 13.2; 2*N*, 16.3; *N*, 20.5; *N*/10, 25.5; *N*/100, 26.1; *N*/1000, 26.2; infinite dilution, 26.2. The hydrations of all the salts used are calculated for infinite dilution, and the following values obtained: potassium chloride, 15; ammonium chloride, 15; lithium chloride, 35; barium chloride, 50. J. F. S.

The Action of Finely Divided Gases. C. ZENGHELIS (*Compt. rend.*, 1920, **170**, 883—885).—The author attributes the action of gases in the nascent state to the fact that they are in an extremely finely divided state. This explanation is based on the fact that he has been able to obtain numerous reductions, such as of solutions of mercuric chloride, potassium chlorate, or potassium

nitrate, or of a saturated aqueous solution of carbon dioxide, by passing hydrogen, generated in an external vessel, into the liquid through filter-paper or dialysis parchment. Under somewhat similar conditions he has performed certain oxidations and brought about the combination of nitrogen and hydrogen in the cold. The reactions are, of course, slower under these conditions than when the nascent gases are used, because the state of division is probably not so fine. W. G.

Catalysis. XIII. Contact Potentials and Dielectric Capacities of Metals, in Relation to the Occlusion of Hydrogen, and Hydrogenation. WILLIAM CUDMORE McCULLAGH LEWIS (T., 1920, 117, 623—638).

Catalytic Oxidation at Solid Surfaces: Some Factors Controlling the Rate of Hydrogenation of Ethylenic Compounds in Presence of Nickel. E. FRANKLAND ARMSTRONG and T. P. HILDITCH (*J. Soc. Chem. Ind.*, 1920, 39, 120—124r).—The hydrogenation of ethyl cinnamate and of anethole in presence of nickel at 140° and 180° takes place at practically a linear rate throughout the greater part of its course, when a free current of hydrogen is maintained. When, however, the reaction is carried out in a closed system, the rate gradually falls off and the curve approximates to the logarithmic type. This is due solely to the decreasing concentration of the hydrogen, caused by the gradual accumulation of gaseous impurities from the hydrogen and, to a less extent, from the organic compound. The results confirm the authors' previous conclusions drawn from a study of the hydrogenation of olive, cottonseed, linseed, and whale oils (A., 1919, ii, 403; this vol., ii, 102). The hydrogenation of anethole gives rise to a crystalline by-product which has not been identified, but ethyl cinnamate is reduced quantitatively to ethyl β -phenylpropionate. E. H. R.

Catalytic Hydrogenation with Protected Hydrosols. ERIC K. RIDEAL (*J. Amer. Chem. Soc.*, 1920, 42, 749—756).—The effect of a protective colloid on the reaction velocity of a hydrogenation process in the presence of colloidal platinum and palladium has been studied, and the results lead to the conclusion that the protecting colloid functions as a peptising agent, in agreement with Bancroft's hypothesis (A., 1917, ii, 129). The addition of a small quantity of a palladium sol to a platinum sol greatly enhances its activity, and it is suggested that promoter action may in part be due to peptisation. The mechanism of catalytic action in the presence of colloidal metal appears to conform rather to the diffusion hypothesis than to the colloid reactant complex theory. Abnormalities are equally explicable on the single-layer theory as on the view that the retardation of diffusion is caused by the products of the reaction. The various reactions were studied by means of the influence of the colloidal metals on solutions of sodium phenylpropionate in the presence of gum arabic. J. F. S.

Rhythmic Mercury-Hydrogen Peroxide Catalysis.

OKAYA (Proc. Phys. Math. Soc. Japan, 1919, [iii], 1, 283—294).—The theory deduced by the author in connexion with the rhythmic precipitation of silver chromate in gelatin and the rhythmic evolution of carbon monoxide during the dehydration of formic acid (A., 1919, ii, 504) has been applied to the rhythmic mercury-hydrogen peroxide catalysis, and verified experimentally. An equation is developed, by means of which the accumulation constants, H' , are shown to be constant throughout the reaction.

CHEMICAL ABSTRACTS.

Structure of Matter and the Quantum Theory. F. H.

LORING (Chem. News, 1920, 120, 181—184, 193—196, 205—207, 217—219).—Atomic weights are derived from that of hydrogen, $H=1.008$, by what is called an "electromagnetic multiplication table":

If	$1 \times 1.008 = 1.008$ (a),
and	$4 \times 1.008 = 4.000$ (d),
then	$2 \times 1.008 = 2.004$ (b),
and	$3 \times 1.008 = 3.002$ (c),

where a =hydrogen; d =helium; b =nitrogen sub-atom; c =fluorine sub-atom. Carbon and oxygen should then be: $C=3He=12.000$; $O=4He=16.000$. Nitrogen and fluorine are: $N=3He+b=14.004$; $F=4He+c=19.002$. The changes of mass in the table are assumed to have their origin in energy changes during the condensation of the constituents of the complex atoms. If helium atoms are assumed as units of atomic structure (4.000), and atomic cutriders, or sub-atoms, a , b , c , d , added, the results are said not to differ appreciably from the accepted atomic weights. The main results obtained in connexion with the quantum theory and positive rays are summarised. The author speculates on atomic structure, isotopes, and valency.

J. R. P.

The Atomic Weight of Hydrogen and its Relation to Prout's Hypothesis.

ALOIS BILECKI (Zeitsch. anorg. Chem., 1920, 110, 335—338).—It has been shown in a previous paper (A., 1917, ii, 197) that the atomic weights of a number of elements are multiples of $n=0.3076923$, where $n=16/52$. It is now shown that $n/40_1=0.007692307$, is a number of fundamental importance. A critical examination of published determinations of the atomic weight of hydrogen ($O=16$) establishes the value 1.0077 for this quantity. The fraction 0.0077, it is pointed out, is almost exactly equal to $n/40$.

E. H. R.

The Atomic Weight of Phosphorus in Relation to that of Silver.

ALOIS BILECKI (Zeitsch. anorg. Chem., 1920, 110, 339—340).—The fundamental number n (preceding abstract) becomes $n_1=0.307350427$ when $Ag=107.88$ instead of 108. The atomic weight of phosphorus, determined through the halogens with respect to $Ag=107.88$, is practically identical with $101n_1=31.04235$.

E. H. R.

The Relation of the Atomic Weight of Barium to that of Silver. ALOIS BILECKI (*Zeitsch. anorg. Chem.*, 1920, **110**, 341—344).—The atomic weight of barium ($A_g=107.88$), 137.37, is practically identical with $447n_1=137.38563$, where $n_1=0.307350427$. When the atomic weight is found by analysis of the bromide, the value found is 0.011%, and by analysis of the chloride, 0.0403% low.
E. H. R.

Radioactive Disintegration of the Atomic Nucleus. HANS TH. WOLFF (*Physikal. Zeitsch.*, 1920, **21**, 175—178).—A theoretical paper in which, accepting the hypothesis of Lindemann (A., 1915, ii, 720) that the instability of the atomic nucleus depends on a large number of particles which move independently inside the nucleus, and assuming that these particles follow Bohr's law in respect of the moment of impulse in their orbital motion, and that the velocity of the α -particle is the same within the nucleus as it is outside, a formula is deduced, from the Geiger-Nuttall relationship between the disintegration constant and the range of the α -particles and from the relationship between the velocity and range of the α -particles, whereby the disintegration constant is expressed as a function of the rotation number of the particles which are expelled as α -rays. A corresponding formula is developed from purely theoretical considerations, and an equation giving the conditions which must hold for both formulae to be identical. The formulae are applied to the case in which the motion of the particles under consideration, undergoes no change during a single step in the disintegration of the atom. J. F. S.

Arrangement of Electrons in the Elements of the Long Periods. R. LADENBURG (*Naturwiss.*, 1919, **8**, 57; from *Chem. Zentr.*, 1920, i, 599—600).—In his previous communication (this vol., ii, 301), the author did not take into account certain definite results obtained by Baerwald in connexion with the irregularities in the atomic volume curve, since they were unknown to him at the time.
H. W.

The Binuclear Atomic Theory and the Disintegration of Nitrogen. O. HINSBERG (*Chem. Zeit.*, 1920, **44**, 294).—The observation of Rutherford (A., 1919, ii, 260) that by bombardment with α -particles from radium-C the nitrogen atom is disintegrated, with the production of rapidly moving hydrogen particles, is in agreement with the author's theory that the elements of the fifth to the eighth groups of the periodic system possess two valency centres (A., 1919, ii, 505). Rutherford considers that the hydrogen nucleus which is separated from the nitrogen atom by the α -particle is situated relatively far from the principal nucleus of the nitrogen atom. In all probability, Rutherford's principal helium-containing nucleus in the nitrogen atom is identical with the author's postulated quadrivalent nucleus, whilst his hydrogen-containing nucleus corresponds with the author's univalent nucleus in the nitrogen atom.
E. H. R.

Absolute Saturation of the Attractive Forces Acting between Atoms and Molecules. M. POLÁNYI (*Zeitsch. Elektrochem.*, 1920, **26**, 161—171).—A theoretical paper in which the absolute saturation of the attractive forces between atoms and molecules is considered. Absolute saturation is defined as follows: If an atom or molecule attracts a molecule AB from infinity with a force F_{AB} , and each of the atoms separately with forces F_A and F_B , respectively, then when $F_{AB} < F_A + F_B$, an absolute saturation of the forces F_A and F_B takes place in the formation of the molecule AB . A number of cases are cited to show that absolute saturation is of common occurrence, among which are included adsorption of gases. It is shown also that in a non-additive field of force, particularly in interatomic and intermolecular fields, which show absolute saturation, the heat of formation of the molecule changes with its position in the field, even when the field is homogeneous. Hence it follows that non-additive fields, which exhibit absolute saturation, can only be produced from hetero-polar systems.

J. F. S.

Barger's Microscopical Method of Determining Molecular Weights. I. The Principle of the Method with Reference to the Molecular and Ionic Attraction of Solute for Solvent. KUMAO YAMAKAMI (*Biochem. J.*, 1920, **14**, 103—113).—It is proved that the force which effects the volume change in the drops is not simply the vapour pressure, but also the osmosis through the thin film of liquid between the drops. When the length of interval between the drops is 2–3 mm., as much as five-sixths or six-sevenths of the volume change is attributable to osmosis. It is therefore possible to measure molecular weights or the degree of association or dissociation by investigating the volume-change of drops which are brought in contact with drops of standard solutions of known molecular concentration.

J. C. D.

Valve for Glass Apparatus. KURT BUNGE (*Chem. Zeit.*, 1920, **44**, 299).—The valve consists of a glass tube melted solid in one spot. On both sides of this are two small holes, not more than 10 mm. apart. A piece of coloured glass marks the position of the valve. A piece of rubber tubing is slipped over the valve, and the latter is operated by gentle pressure by the thumb and forefinger on the rubber. The valve may be used on burettes, or on pipettes to prevent liquid entering the mouth.

J. R. P.

Effective Connecting Bulb. C. M. CLARK (*J. Ind. Eng. Chem.*, 1920, **12**, 366).—A bulb tube for preventing spray passing from a distillation flask into the receiver consists of a simple bulb on a tube, but the bulb has an internal baffle-plate in the form of a deep, inverted watch-glass; the latter is attached to the end of the upper tube (this end extends a short distance into the bulb), and the edge of the baffle-plate reaches to within 5 mm. of the side of the bulb.

W. P. S.

Manometer for Vacuum Distillation. H. T. CLARKE (*J. Amer. Chem. Soc.*, 1920, **42**, 786).—A manometer is described, for use in vacuum distillation, which is designed to prevent liquid passing into the exhausted limb and also to prevent breakage if air should suddenly enter the distillation apparatus. The modification consists in the introduction of a hook-shaped trap half-way up the evacuated limb. The trap consists of a very fine capillary tube widened at one end and sealed to the walls of the manometer tube. This effectually prevents moisture getting into the exhausted space, and if the pressure suddenly drops it prevents the mercury rushing in and breaking the top of the manometer tube. J. F. S.

A Device for Regulating the Temperature of Incubators either above or below Room Temperature. JOHN H. NORTHROP (*J. Gen. Physiol.*, 1920, **2**, 309—311).—The water flow through the jacket of a double-walled incubator is regulated by causing a relay to direct a stream of water either through the incubator or to waste as required by the temperature changes. This is brought about by means of a wire attached to the armature of the relay and attached at the other end to a glass pipette at the end of a vertical rubber tube. The current necessary to move this wire and pipette is so small that it is unnecessary to use a secondary circuit. The regulator may be either of the mercury-toluene or bimetallic type. J. C. D.

Inorganic Chemistry.

Generation of Hydrogen by the Reaction between Ferrosilicon and Sodium Hydroxide Solution. E. R. WEAVER (*J. Ind. Eng. Chem.*, 1920, **12**, 232—240).—The preparation of hydrogen from ferrosilicon, sodium hydroxide, and water is most economically effected by dissolving sodium hydroxide in water so as to form a 20—30% solution, mixing a portion of this solution and ferrosilicon in the reaction chamber, and when the temperature has reached 0° adding ferrosilicon and the remainder of the sodium hydroxide solution at a uniform rate in order to keep the temperature constant. About equal weights of ferrosilicon and sodium hydroxide may be used. Towards the end of the operation, the reaction mixture is cooled by means of an internal spray of water. W. P. S.

The Constitution of Hydrogen Peroxide. ANTONIO RUIZ y MIRÓ (*Helv. Chim. Acta*, 1920, **3**, 347—365).—The validity of Willstätter and Hauenstein's argument against the unsymmetrical formulae for hydrogen peroxide (*A.*, 1909, ii, 566), based on the reduction of benzoyl peroxide to benzoic acid as distinguished from

benzoic anhydride, is weakened by the fact that water formed in the reaction might hydrolyse any anhydride formed. The same result has now been obtained, however, by reduction in boiling benzene solution with yellow phosphorus. In addition, potassium orthophosphate is the sole product of the reduction of potassium perphosphate by potassium iodide in acetic acid solution, or by ferrous or cobalt hydroxides in alkaline solution. It is also shown that sulphuric acid cannot be oxidised to persulphuric acid by permanganic acid, plumbic salts, or nickel peroxide. The majority of oxidations due to hydrogen peroxide are really hydroxylations, but, although this is contrary to the asymmetrical formula, the case of potassium permanganate shows it does not necessarily lead to the symmetrical formula. This formula does not explain the reducing properties of hydrogen peroxide, which the author attributes to weakly-bound hydrogen atoms. By anodic oxidation of solutions of potassium hydroxide containing potassium fluoride, up to 5.35% of hydrogen peroxide, calculated on the energy expended, was obtained (compare Riesenfeld and Reinhold, A., 1909, ii, 879). The action of ozone on fuming sulphuric acid (Schmidlin and Massini, A., 1910, ii, 498) and of perchromic acid on hydrogen peroxide were also examined, evidence of interaction being obtained in the latter case (compare Riesenfeld, A., 1909, ii, 51). The author suggests the

formula $\begin{array}{c} \text{H} \\ \diagup \quad \diagdown \\ \text{O} \cdots \cdots \text{O} \\ \diagdown \quad \diagup \\ \text{H} \end{array}$ for hydrogen peroxide, and proposes that per-

oxides of the general type RO_2R be called anhydro-hydroperoxides, to distinguish them from Baeyer's hydroperoxides, RO_2H . As a test for hydroperoxides which can only be examined in acid solution, and to which Riesenfeld and Mair's test cannot therefore be applied (A., 1912, ii, 156), hydrogen peroxide itself is suggested. One molecule of oxygen is liberated, whilst the anhydroperoxides merely form an additive product.

J. K.

Viscosity of Sulphur. C. COLERIDGE FARR and D. B. MACLEOD (*Proc. Roy. Soc.*, 1920, [A], 97, 80—98).—The viscosity of molten sulphur has been determined at a series of temperatures by the method of rotating cylinders. It is shown that the viscosity of twice distilled, but not gas-free, sulphur has the value 0.1094 C.G.S. units at 123°, and from this temperature it falls to a minimum of 0.0709 C.G.S. units at 150° and then rises to 0.0759 at 159°, when the rise becomes more marked, but nothing of the nature of a strict transition point is observed. Exposure to air in the molten condition, especially below 160°, has a marked effect on the viscosity from 160° upwards. The effect is a slow one, the viscosity continuing to rise for as much as forty-eight hours on exposure to the air for that time. The maximum for purified gas-free sulphur is reached at 200°, when the value is 215 C.G.S. units; the maximum for purified but not gas-free sulphur, after a long exposure to air, is reached at 190°, and has a value about 800 C.G.S. units. Crystallisation has an apparent, but probably

secondary, effect on the viscosity as measured at any temperature. It apparently raises the viscosity of a low-valued sample of sulphur and lowers the viscosity of a high-valued sample. The effect of crystallisation seems to disappear when the viscosity of the sample is about 300 *C.G.S.* units at 171°. Sulphuric acid appears to be the impurity which, after exposure to the air, causes the extreme variations which are found in the values of the viscosity of air-exposed sulphur. Changes in the viscosity are accompanied by a corresponding change in the amount of insoluble sulphur present.

J. F. S.

A New Hydrogen Sulphide Generator. BERTRAM DILLON STEELE and HENRY GEORGE DENHAM (*T.*, 1920, 117, 527—529).

Solubility of Gases in Water. Sulphur Dioxide. FREESE (*Chem. Zeit.*, 1920, 44, 294).—Determinations of the solubility of sulphur dioxide in water between 0° and 40° at 760 mm. have been made, and the results are given in grams and in litres of gas dissolved per litre of water. At 0° the solubility is 228.29, at 10° 162.09, at 20° 112.90, at 25° 94.08, at 30° 78.67, and at 40° 54.11 grams per litre.

E. H. R.

Catalytic Synthesis of Ammonia. M. GUICHARD, VAVON, CORNEC, CANTRAGREL, STEVENSON, APARD, and BOURDIOL (*Bull. Soc. d'Encour.*, 1920, 132, 71—102).—The authors have investigated the catalytic manufacture of ammonia, especially as regards the suitability of various catalysts. Addition of magnesia or alumina greatly increases the life of catalysts, such as iron, cobalt, nickel, tungsten, and molybdenum, and a combination of two of these metals ensures greater catalytic efficiency. Iron-molybdenum was proved to be the most resistant and to give the highest ammonia concentration—more than 4%. Iron alone gave less than 1%, molybdenum less than 1.5%, nickel 3%, and cobalt 3%. The best method of preparation is by precipitation of ferric nitrate with ammonium molybdate, followed by ignition, and subsequent reduction. With perfectly dry gases, uranium is a suitable catalyst, but its combinations with cobalt and molybdenum are inferior. Uranium-nickel gives poor results, and uranium-tungsten is practically inert. The authors have made a partial study of the whole cycle of operations, including the circulation of the gases, the recovery of heat, absorption of ammonia under pressure, and the most suitable arrangement of the furnace. [See further, *J. Soc. Chem. Ind.*, 1920, 362A.]

W. J. W.

Vapour Pressure of Ammonia. C. S. CRAGG, C. H. MEYERS and C. S. TAYLOR (*J. Amer. Chem. Soc.*, 1920, 42, 206—229).—The vapour pressure of ammonia has been determined over the temperature range -78° to +70° by the manometric method. Several forms of manometer are described in the paper. Several different samples of ammonia were used in the experiments, and these contained less than 1 part per 100,000 parts of non-con-

densing gas and less than 0.01% by weight of other impurities. The phenomenon of hysteresis was observed near the boiling point of ammonia with a commercial specimen which contained a small amount of air; this indicates the absolute necessity of very complete removal of dissolved gases for any accurate measurements of vapour pressure by the static method. The normal boiling point of ammonia was determined by both the static and the dynamic method, and the mean of the two results found to be -33.35° . Empirical equations are deduced which represent the vapour pressure over the measured range; the results of 122 measurements between -78° and $+25^{\circ}$ agree with the values calculated by means of these equations to within 1 millimetre, and the results of 28 measurements between $+25^{\circ}$ and $+70^{\circ}$, made with a calibrated piston gauge, agree to within 3 millimetres. The vapour pressure of ammonia is expressed between -80° and $+70^{\circ}$ by either of the equations $\log_{10} p = 30.256818 - 1914.9569/\theta - 8.4598324 \log_{10} \theta + 2.39309 \times 10^{-3} \theta + 2.955214 \times 10^{-8} \theta^2$ or $\log_{10} p = 12.465400 - 1648.6068/\theta - 0.01638646\theta + 2.403276 \times 10^{-5} \theta^2 - 1.168708 \times 10^{-6} \theta^3$, where p is expressed in millimetres of mercury and θ in degrees absolute (abs. degrees = $^{\circ}\text{C} + 273.1$). The slope of the vapour pressure-temperature curve is obtained by differentiation of either of the above equations.

J. F. S.

Preparation of Mixtures of Nitrogen and Hydrogen by Decomposition of Ammonia. R. O. E. DAVIS and L. B. OLMSTEAD (*J. Ind. Eng. Chem.*, 1920, **12**, 316—317).—The catalytic decomposition of ammonia by heat in the presence of iron, first investigated by Ramsay and Young (*T.*, 1884, **45**, 88), and subsequently by Perman and Atkinson (*Proc. Roy. Soc.*, 1905, **74**, 110), has been studied under manufacturing conditions, an electrically heated iron autoclave packed with iron turnings being used for the purpose. At 370° , 73% of the ammonia was decomposed, at 470° 84%, at 540° 94%, at 650° 99.6%, and at 735° 99.7%. In practice, about 100 cu. ft. per hour of the mixture of hydrogen and nitrogen could be obtained at 675° with a loss of 0.3 to 0.4% of ammonia. The equilibrium of a system $\text{H}_2\text{--N}_2\text{--NH}_3$ at that temperature corresponds with about 0.02% of ammonia. The average time of contact was about five seconds. When copper was used as the catalyst, a temperature about 200° higher and longer contact were required, which is in accordance with the facts observed by Beilby and Henderson (*T.*, 1901, **79**, 1245). [See, further, *J. Soc. Chem. Ind.*, 1920, 362A.]

C. A. M.

The Discoverer of Phosphorus. LUCIANO P. J. PALET (*Anal. Soc. Quim. Argentina*, 1917, **5**, 238—243).—In chemical literature, the discoverer of cobalt is sometimes mistaken for the discoverer of phosphorus, or at least their names are spelt in the same manner (Brandt). The German alchemist Brand (born 1625) discovered phosphorus in the year 1669, 1674, or 1677, whilst the discovery of cobalt was made (1733 or 1735) by the Swedish chemist Brandt (1694—1798) (compare A., 1919, ii, 511).

W. R. S.

Preparation of Arsenic Trichloride from White Arsenic and Carbonyl Chloride. L. H. MILLIGAN, W. A. BAUDE, and H. G. BOYD (*J. Ind. Eng. Chem.*, 1920, **12**, 221—223).—When carbonyl chloride is passed over a mixture of arsenic trioxide (80%) and carbon (20%) heated at 200° to 260°, arsenic trichloride is formed, the yield being almost quantitative. The method has been used as a means of utilising the impure "tail gas" from carbonyl chloride manufacture. It is probable that the treatment of inorganic compounds with carbonyl chloride in the presence of carbon as a catalyst may be used as a general method of chlorination. W. P. S.

Reversible Oxidation of Arsenious Acid. C. MATIGNON and J. ALLAIN LECANU (*Compt. rend.*, 1920, **170**, 941—943).—When arsenious oxide is heated with oxygen at temperatures varying from 400° to 480° and pressures of 127—180 atmos., a certain amount of oxidation occurs, the extent of oxidation, other things being equal, increasing with the temperature. Similarly, a concentrated solution of arsenious oxide in aqueous sodium hydroxide at 80° under a pressure of oxygen equal to 50 atmos. is oxidised to the extent of 10.9% in five hours. W. G.

The Disposition of the Atoms and the Optical Rotation of Quartz and Sodium Chlorate. J. BECKENKAMP (*Zeitsch. anorg. Chem.*, 1920, **110**, 290—310).—The structures suggested by previous workers for quartz, for example, those of Söhncke and Bragg, do not account for optical rotation in directions perpendicular to the principal axis. In the structure now proposed, the silicon atoms form a rhombohedral lattice instead of a three-point screw system, as in Bragg's structure. The spiral structure only appears after the introduction of the oxygen atoms, when the total structure is seen to be composed of nine three-sided, prismatic lattices. The disposition of the oxygen atoms is such that the orientation of the valency directions is the same in horizontal or vertical molecular layers, and the optical rotation perpendicular to the vertical axis is then accounted for. The different kinds of twin crystals of quartz, and the relation of quartz to tridymite, β -quartz, and cristoballite, are discussed. Sodium chlorate has a structure similar to that ascribed by Bragg to calcite, the calcium atoms being replaced by sodium and the carbon by chlorine. E. H. R.

Luminous Carbon Flames Regarded as Turbid Media. HERMANN SENFTLEBEN and ELISABETH BENEDICT (*Kolloid Zeitsch.*, 1920, **26**, 97—100).—When an intense beam of light from an arc is projected on to a Hefner candle flame, the beam is bent from its original path and polarised. The authors have measured the amount of deflexion, the polarisation, and the intensity of the deflected beam. It is shown that the intensity of the deflected light varies strongly with the direction, in the sense that with increasing angle between the incident beam and the direction of

measurement it increases, for example, a change in the angle from 45° to 140° changes the intensity 300%. The fraction of the light which is polarised reaches a very definite maximum when the angle of observation is 90° to the incident light. At this angle, the fraction is 86%. The intensity of the deflected beam increases with decreasing wave-length; thus there is an increase in intensity of 150% as the wave-length changes from $0.700\ \mu$ to $0.475\ \mu$. The experiments show that the carbon flame behaves in a manner analogous to that of a turbid medium.

J. F. S.

Removal of Carbon Monoxide from Air. ARTHUR B. LAMB, WILLIAM C. BRAY, and J. C. W. FRAZER (*J. Ind. Eng. Chem.*, 1920, 12, 213—221).—Of various absorbents and catalytic oxidising substances examined, a mixture of MnO_2 , 50%; CuO , 30%; Co_2O_3 , 15%; and Ag_2O , 5%, gave the best results. The silver oxide was precipitated in the moist mixture of the other oxides, the mass then dried and ground to size. This mixture acts indefinitely at the ordinary temperature against any concentration of carbon monoxide in air, provided that the air is dry. When used in gas-mask canisters, the latter must be provided with a calcium chloride drying chamber at the inlet, and the "life" of the canister is then limited solely by that of the drier.

W. P. S.

Constitution of Carbon Sub-oxide. II. STANLEY REDGROVE (*Chem. News*, 1920, 120, 209—210).—By means of a method of calculation due to the author, the following theoretical numbers are found: for $\text{O}:\text{C}:\text{C}:\text{C}:\text{O}$, mol. heat of combustion, 243.6 Cal.;

mol. heat of formation, 47.4 Cal.; for $\text{C} \begin{array}{c} \diagup \text{O} \diagdown \\ \diagdown \text{O} \diagup \end{array} \text{C}:\text{O}$, mol. heat of

combustion, 286.1 Cal.; mol. heat of formation, 4.8 Cal. A determination of the thermochemical data would enable the constitution of the compound to be settled.

J. R. P.

Carbonyl Chloride. III. Action of Carbonyl Chloride on Industrial Iron Containers. M. DELÉPINE and L. VILLE (*Bull. Soc. chim.*, 1920, [iv], 27, 288—290).—When it contains a little free chlorine, carbonyl chloride slowly attacks iron, and the resulting ferric chloride colours the carbonyl chloride yellow. The oxychloride free from chlorine will dissolve rust or the sub-carbonate of iron, and it is probably from this source that the ferric chloride in commercial carbonyl chloride comes.

W. G.

Phase Diagram of Potassium and Sodium Chlorides and their Etched Figures. G. TAMMANN (*Nachr. Ges. Wiss. Göttingen*, 1919, 422—427; from *Chem. Zentr.*, 1920, i, 604).—Potassium and sodium chlorides form a continuous series of mixed crystals between 660° and 500° . Since neither salt has a transition point, the phenomena observed when the mixed crystals are cooled must be attributed to separation of the components. With diminishing temperature, therefore, either the attractive forces within

the molecules of the respective chlorides must increase, or those between the unlike molecules must be greatly weakened. The results obtained by etching the individual crystals at the ordinary temperature indicate that the intra-molecular forces of the potassium chloride crystal differ from those of the sodium chloride crystal, or, more precisely, that certain lattice regions are more closely united in the former, whilst such differences are not observed in the latter. In the light of these observations, it is surprising that Röntgen analysis indicates the same lattice for each crystal. A possible explanation of the etched figures, based on atomic lattice structure, is discussed.

H. W.

Preparation of Sodium Amalgam in Flakes. ARTHUR I. HIRSCHFELDER and MERRILL C. HART (*J. Ind. Eng. Chem.*, 1920, 12, 499).—To obtain sodium amalgam in readily pulverisable form the hot liquid amalgam is slowly poured into a vessel in which xylene or petroleum is mechanically agitated. The resulting flocculent deposit is dried on porous porcelain in a current of air.

C. A. M.

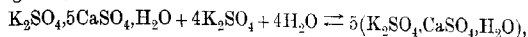
The Variations in the Composition of Ammonium Phosphomolybdate. S. POSTERNAK (*Compt. rend.*, 1920, 170, 930—933).—Ammonium phosphomolybdate precipitated from phosphate solutions in the absence of ammonium salts always contains phosphorus and molybdenic oxide in a constant ratio. It consists of a variable mixture of di- and tri-ammonium phosphomolybdates, varying according to the composition of the ammonium molybdate solution used.

In the presence of 5% or more of ammonium nitrate or sulphate the phosphomolybdate precipitate obtained is a complex mixture of the types $16(\text{NH}_4)_3(\text{MoO}_3)_{12}\text{PO}_4\cdot\text{NH}_3(\text{MoO}_3)_4\text{NO}_3$ and $8(\text{NH}_4)_2(\text{MoO}_4)_{12}\text{PO}_4\cdot(\text{NH}_4)_2(\text{MoO}_3)_8\text{SO}_4$ respectively. In all cases the molybdenic acid behaves as though, in acid medium, it existed in the tetramolybdenic state, and in this form combined with the hydroxyl groups of all the mineral acids present. This supports Kehrman's view as to the constitution of phosphomolybdenic acid (compare A., 1887, 777).

W. G.

Formation of the Double Salts of Calcium and Potassium Sulphates at 100°. EVALD ANDERSON and R. J. NESTELL (*J. Ind. Eng. Chem.*, 1920, 12, 243—246).—In determining the conditions of equilibrium for the formation of syngenite ($\text{K}_2\text{SO}_4\cdot\text{CaSO}_4\cdot\text{H}_2\text{O}$) and potassium pentacalcium sulphate at 100°, known weights of potassium sulphate and gypsum were shaken seven to twenty-three days with water in bottles immersed in boiling water, the resulting solutions rapidly filtered, and the potassium and calcium oxides and sulphuric anhydride estimated. Experiments were also made with previously prepared syngenite and potassium pentacalcium sulphate. The mean results showed that for the formation of the latter salt as in the equation $5(\text{CaSO}_4\cdot 2\text{H}_2\text{O}) + \text{K}_2\text{SO}_4 = \text{K}_2\text{SO}_4\cdot 5\text{CaSO}_4\cdot \text{H}_2\text{O} + 9\text{H}_2\text{O}$, the equilibrium concentration for

potassium sulphate was 1.05 mols., and for the calcium sulphate 0.24 mol., per 1000 mols. of water. For the formation of the syngenite,



the equilibrium concentrations were 9.26 mols. of potassium sulphate and 0.142 mol. of calcium sulphate per 1000 mols. of water at 100°. These figures are considerably lower than those obtained by extrapolation from the results of D'Ans at 83°. Hence the value given by D'Ans for potassium sulphate is too high, or the equilibrium curve has a maximum between 83° and 100°.

C. A. M.

Calcium Arsenates. I. Equilibrium in the System Arsenic Oxide, Calcium Oxide, Water at 35° (Acid Section). C. M. SMITH (*J. Amer. Chem. Soc.*, 1920, **42**, 259—265)

—The equilibrium conditions between arsenic oxide, calcium oxide, and water have been determined at 35° for those mixtures in which the arsenic oxide is in excess and from which acid arsenates are likely to be produced. The results are recorded in a diagram to represent the phase rule relationships. Two compounds are found to be stable under the experimental conditions, dicalcium orthoarsenate monohydrate, $\text{CaHAsO}_4, \text{H}_2\text{O}$, which is identical with the mineral haidingerite, and monocalcium orthoarsenate, $\text{CaH}_4(\text{AsO}_4)_2$, which exist below and above, respectively, an acid concentration corresponding with 27.5% of arsenic oxide.

J. F. S.

Atomic Weight of Radio-lead. R. DE MONTESSUS DE BALLORE (*Rev. gen. Sci. pure et appl.*, 1919, **30**, 673; from *Chem. Zentr.*, 1920, i, 558).—The figure 206 has been proposed for this atomic weight; a much more probable value is 206.5 ± 0.05 .

H. W.

Micrometallurgy. ST. BOGDAN (*Bul. Soc. Chim. România*, 1919, **1**, 60—72).—A micrographic study of the alloys of copper and silicon and iron and silicon. In all such alloys, when the percentage of silicon is very small, the result is a homogeneous solid solution. If the amount of silicon present exceeds 1%, crystalline compounds, embedded in the solid solution of the alloy, are always obtained, and are probably silicides. When the silicon content exceeds 4%, two crystalline silicides can be isolated, and also silicon in a crystalline and in an amorphous state. Prolonged heating of the alloys at high temperatures facilitates the separation of their components. As the proportion of silicon present increases further, the mass becomes more crystalline, the hardness increasing, the alloy becoming more friable.

W. G.

Copper-Aluminium-Zinc Alloys of High Zinc Content. E. H. SCHULZ and M. WAHLERT (*Metall. und Erz.* 1919, **16**, 170—176, 195—201).—The thermal, structural, and mechanical properties of copper-aluminium-zinc alloys containing up to 10%

of copper and 10% of aluminium were investigated. Five sections of the three-dimensional equilibrium diagram are given, representing, respectively, alloys containing 2%, 4%, 6%, 8%, and 10% of copper with a varying aluminium content. A reproduction of the complete space diagram is also given, the principal features of which are two broad, curved surfaces intersecting in a eutectic line at 375° , running approximately parallel to the copper co-ordinate, and a second line, corresponding with 1.9% of copper, parallel to the aluminium co-ordinate, dividing the diagram into two unequal sections. The microscopic structure of the alloys confirms the conclusions drawn from their thermal study. Alloys containing less than 1.9% of copper and less than 0.75% of aluminium consist of homogeneous ternary mixed crystals. Those with more than 1.9% of copper and up to 0.8% of aluminium consist of a solid solution of ϵ -crystals of the zinc-copper series with α -aluminium crystals. The remainder of the alloys fall into five groups, according to the thermal equilibrium diagram, but only four of these can be distinguished by their structure.

The mechanical properties studied were the hardness, tensile strength, and crushing strength. No relation could be found between the tensile strength and the equilibrium diagram. The curves of equal hardness and of equal crushing strength, however, show an inflexion at a point which appears to correspond with the limit of solubility of zinc crystals in the alloys. E. H. R.

Mechanism of the Formation and the Properties of Mercury Hydrosols prepared by Various Methods of Dispersion. IVAR NORDLUND (*Kolloid Zeitsch.*, 1920, 26, 121—138).—Methods of preparing mercury sols by various methods are described. The methods are subdivided into three groups: (i) mechanical dispersion, (ii) thermal dispersion, and (iii) electrical dispersion. Mercury sols of small stability are produced when a fine stream of mercury is allowed to fall into a solution of potassium citrate ($0.5-5 \times 10^{-3}N$) or a solution of gelatin (0.1%) with a velocity of 100 metres per second. In the latter case, a black coagulum is obtained, which consists of highly dispersed mercury and gelatin, and is readily peptised by warming with a trace of alkali to form a grey sol. Shaking mercury with conductivity water produces a very little of a rapidly sedimenting sol; the addition of potassium chloride, sodium chloride, potassium nitrate, potassium sulphate, copper sulphate, mercurous nitrate, and acetic acid to the water did not increase the sol formation. The presence of ammonia ($1 \times 10^{-3}N$) in the water produced a sol which was not very stable, complete sedimentation occurring in two or three days. Ammonium chloride and sulphate solutions shaken with mercury produced sols which, in the case of ammonium chloride, were much more stable than in any of the previous cases. Shaking with a solution of potassium citrate ($2-7 \times 10^{-3}N$) produced a very concentrated sol, which was coagulated by higher concentrations of citrate. This sol has a strong reddish-brown-grey colour, and is very stable. It may be kept for months without

coagulating. Shaking with solutions of carbamide (0.01%) and gelatin (0.0001—0.0025%) produced a dilute, grey sol. The formation of sols by the "spiriting" method is held to be due to a spontaneous atomising of the rushing mercury stream and to the atomising of the larger drops against the walls of the vessel. In the shaking experiments, the formation of sols is due to the disintegration of thin laminae of mercury; the bursting of mercury bubbles has little effect in sol formation. A deep brown, very concentrated sol was formed by distilling mercury from a porcelain retort through a red-hot silica tube, and thence through a fine jet into cold water. The mercury vapour entered the water with a velocity of 160 metres per second. The sol is not very stable, and in ten to fifteen minutes it had lost its brown colour, and in two or three days it had completely and irreversibly coagulated. Experiments, of the type often described, by electrical dispersion, both with direct and alternating current arcs, are also described. The partition of the radii of the particles has been worked out for the more stable of the sols described.

J. F. S.

Compounds of Oxides. (MLCE) S. VEIL (*Compt. rend.*, 1920, 170, 939—941).—Mixtures of ceric and chromic oxides in different molecular proportions were compressed and heated by methods similar to those used for alloys. The electrical conductivity at high temperatures and the coefficients of magnetisation at the ordinary temperature were then determined in each case. The curves showing the results indicate the existence of the compounds $\text{CeO}_2\cdot\text{Cr}_2\text{O}_3$, $3\text{CeO}_2\cdot 4\text{Cr}_2\text{O}_3$, $\text{CeO}_2\cdot 2\text{Cr}_2\text{O}_3$, and $\text{CeO}_2\cdot 5\text{Cr}_2\text{O}_3$, and the probable existence of the compounds $5\text{CeO}_2\cdot\text{Cr}_2\text{O}_3$, $7\text{CeO}_2\cdot 4\text{Cr}_2\text{O}_3$, and $\text{CeO}_2\cdot 9\text{Cr}_2\text{O}_3$.

W. G.

The Reaction between Hydrochloric Acid and Potassium Permanganate. F. P. VENABLE and D. H. JACKSON (*J. Amer. Chem. Soc.*, 1920, 42, 237—239).—It is shown that the reaction between potassium permanganate and hydrochloric acid and hydrobromic acid, respectively, takes place in two stages, which may, by regulating the quantity of acid employed, be separated. The reaction is represented: (i) $2\text{KMnO}_4 + 8\text{HCl} = 2\text{KCl} + 2\text{MnO}_2 + 4\text{H}_2\text{O} + 3\text{Cl}_2$; (ii) $\text{MnO}_2 + 4\text{HCl} = \text{MnCl}_2 + 2\text{H}_2\text{O} + \text{Cl}_2$. It is also shown that hydrobromic acid reacts at a concentration 0.00154*N*, whilst with hydrochloric acid no reaction takes place until the concentration reaches 0.002*N*.

J. F. S.

System Hydrated Ferric Oxide-Arsenious Acid. WILHELM BILTZ (*Kolloid. Zeitsch.*, 1920, 26, 179—180).—A criticism of Öryng's paper (*A.*, 1918, ii, 317) on the adsorption compounds of ferric arsenite. Compare also Biltz and Utescher (*A.*, 1905, ii, 807).

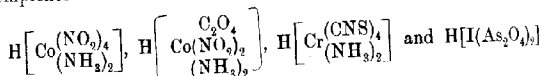
J. F. S.

Influence of Superimposed Alternating Current on the Anodic Formation of Ferrates. G. GRUBE and H. GMELIN (*Zeitsch. Elektrochem.*, 1920, 26, 153—161).—An investigation of

conditions under which sodium ferrate is formed by anodic oxidation in concentrated sodium hydroxide. It is shown that increasing temperature and alkali concentration favour large yields. With increasing current density the yield increases to a maximum, and then falls with any further increase in the current density. The current yield of sodium ferrate can be considerably increased by superimposing an alternating current over the direct current. The increase in the yield, for constant direct current, reaches a maximum for a definite alternating current density. Using as electrolyte 40% sodium hydroxide with an iron anode and a platinum cathode and electrolysis at 35° with a direct current of 3.33 amps./sq. dm. and an alternating current of 5.0 amps./sq. dm., an increase of 160% in the yield of sodium ferrate is obtained. In the preparation of concentrated solutions of ferrates the anode and cathode must be separated, and since ferrates lose oxygen at 50° and precipitate ferric hydroxide, this temperature must not be exceeded in the preparation, and the velocity of formation must be increased by imposing an alternating current on the direct current. In this way undecomposed saturated solutions and the crystalline salts may be obtained.

J. F. S.

The Nature of Subsidiary Valencies. XXIV. Salts with High Ammonia Content. FRITZ EPHRAIM and FRANZ MOSER (*Ber.*, 1920, **53**, [B], 548—563).—Recently, the addition of ammonia to salts containing a particularly large anion united to a small cation has been investigated, and it has been shown that amines with unusually high ammonia content are thereby formed (*A.*, 1918, i, 389). In the previous communication, salts of organic acids were employed, but it is now shown that suitable inorganic complexes behave in a similar manner, and amines of the acids



are now described. Addition of ammonia proceeds in many cases beyond the octamine stage, and, in extreme cases, leads to the liquefaction of the salts. The colour of the highly ammoniated compounds does not differ markedly from that of the hexamines, and the volume does not greatly increase when ammonia is added beyond the hexamine stage, whilst, also, reaction occurs without any great development of heat. The higher amines do not exhibit a step-wise degradation to lower amines with rise of temperature, but, generally speaking, gradually evolve ammonia in much the same manner as does a solid solution or adsorption compound.

The author extends his previous theory (*loc. cit.*) on the influence of the relative size of anion and cation on the properties of the salt. The presence of neutral portions (water, etc.) is supposed in a manner to fill the seams of the crystal caused by the unequal pairing of anion and cation, and thus to stabilise the whole structure. Addition of water as "packing material" increases the likeness of the

salt to water, and hence the solubility in water. The most sparingly soluble salts are therefore to be expected among such as contain most equally matched anion and cation; in general, the cation is spatially greater than the anion, the largest of the latter being represented by the alkali metals, particularly caesium; with voluminous anions (perchlorate, platinichloride, etc.) it is precisely this metal which forms the relatively least soluble salts, whilst the corresponding salts of other metals only crystallise after enlargement of the cation by the addition of neutral substances. Conversely, bulky basic radicles are best precipitated by acid radicles of compact structure (ClO_4 , PtCl_6 , picric acid), quite apart from any question of basic character.

The following individual salts are described which, in general, are prepared by mixing suitable components in the presence of ammonia:

Tetranitritodiamminocobalti-compounds, $[\text{Co}(\text{NO}_2)_4(\text{NH}_3)_2]\text{M}$.—Nickel: *hexammine* and *octammine*. Copper: *tetrammine* (+ H_2O), olive-green, microscopic prisms, and *octammine*. Zinc: *pentammine* and (?) *hexammine*.

Oxalodinitritodiamminocobalti-compounds.—Nickel: *octammine*, stable at the ordinary temperature; *decammine*, formed at -13° , and, possibly, *dodecammine* at still lower temperature. Copper: *tetrammine*, red needles, which did not further absorb ammonia at -18° . Zinc: *tetrammine*, *hexammine*, and *octammine*. Cadmium: *tetrammine*, pale red crystals which do not absorb ammonia.

Tetrathiocyanatodiamminochromi-compounds.—Nickel: *tetrammine*, which passes into the *nonammine* at the ordinary temperature and becomes completely liquefied when treated with ammonia at -20° . Copper: (?) *tetrammine* and *octammine*. Cadmium: *decammine*, which becomes partly liquid when treated with excess of ammonia at -20° . Zinc: *monammine*, *octammine*.

Compounds derived from $\text{II}[\text{I}(\text{As}_2\text{O}_3)]$ (compare Weinland and Gruhl, A., 1919, ii, 411).—Zinc: *heptammine*, which passes through a series of solid solutions to the *hexammine* (at 70°), which is converted to the *tetrammine* (at 87°); the latter is stable up to 200° , but at 210° passes into the *diammine*. Nickel: one molecule of salt combines with the following numbers of molecules of ammonia: 16.1 at -20° ; 14.2 at $+18^\circ$; 10.3 at 66° ; 1.2 at 77° .

Attempts to obtain disulphitetetramminocobalti-, heptanitrososulphonicferri-, and dinitrosothiosulphatoferri-salts of the heavy metals were unsuccessful. Salts such as copper metachloroantimonate are decomposed by ammonia into their components, which then separately absorb the gas.

H. W.

Reversible Reactions of Water on Tungsten and its Oxides. GEORGES CHAUDRON (*Compt. rend.*, 1920, 170, 1056—1058).—At 850° the two reversible reactions may be expressed by $\text{W} + 2\text{H}_2\text{O} \rightleftharpoons \text{WO}_3 + 2\text{H}_2 + \text{L}_{850}$ and $2\text{WO}_3 + \text{H}_2\text{O} \rightleftharpoons \text{W}_2\text{O}_7 + \text{H}_2 + \text{L}_{850}$. The value of L_{850} for the first reaction is 2×4.4 Cal., and for the second 4 Cal.

W. G.

Solubility in the Solid State of Tin in Lead. N. PARRAVANO and A. SCORTECCI (*Gazzetta*, 1920, 50, i, 83—92).—In view of the discordance between the values given by different investigators for the solubility of tin in lead in the solid state (compare Rosenhain and Tucker, A., 1908, ii, 1038; Degens, A., 1909, ii, 888; Mazzotto, A., 1911 ii, 889; Parravano and Sirovich, A., 1912, ii, 846; Guertler, *Metallographie*, 736, and *Zeitsch. anorg. Chem.*, 1916, 98, 97), the authors have measured the electrical conductivities of a series of nineteen tin-lead alloys at various temperatures lying between that of the air and that of the eutectic alloy.

The conductivity isotherms are found to consist of two branches, that in the neighbourhood of the lead axis indicating the existence of solid solutions. The limits of miscibility in the solid state of tin in lead, corresponding with the points of intersection of the two branches, show that the percentages of tin in the saturated solutions at different temperatures are as follows: 14.5 at 175°; 13.5 at 170°; 12.5 at 162°; 10 at 150°; 6.5 at 100°; 5.0 at 75°; 3.0 at 50°; and 1.5 at 25°. These values differ considerably from those given by Rosenhain and Tucker and from those assumed by Guertler, the first three of them being in moderately good agreement with Mazzotto's figures.

The curve along which tin separates from its solid solutions in lead at temperatures below the eutectic temperature is very regular, and confirms the conclusion that the recalescence observed with the solid alloys is due to a simple supersaturation phenomenon.

T. H. P.

Colloidal Rhodium. C. ZENGHELIS and B. PAPACONSTANTINOU (*Compt. rend.*, 1920, 170, 1058—1061).—Colloidal rhodium may best be prepared by the following process. The metallic rhodium, after suitable purification, is converted into the double chloride, $\text{Na}_2\text{Rh}_2\text{Cl}_{12}$. This is dissolved in water, and to the slightly alkaline solution a solution of sodium protalbate is added and then a suitable reducing agent. Of the reducing agents tried, formaldehyde at 40° in a slightly alkaline solution is the most satisfactory, and under these conditions a clear, colloidal solution of rhodium is obtained. On purification by dialysis and subsequent evaporation to dryness in a vacuum, ebony-black plates are obtained which contain 33% of rhodium.

The colloidal solution of rhodium absorbs hydrogen to the extent of 2510—2960 times the volume of rhodium present. Similarly, the rhodium absorbs 346 times its volume of carbon monoxide at 12—14° and 1820 times its volume at 60°. The colloidal solution, slightly alkaline, causes a very slight combination of nitrogen and hydrogen to give ammonia, the reaction being considerably enhanced if the solution is made just acid with very dilute tartaric acid in the presence of potassium tartrate.

W. G.

Mineralogical Chemistry.

Colouring Matters of Red and Blue Fluorite. CECIL STEVENSON GARNETT (T., 1920, 117, 620—622).

Aphthitalite (= Glaserite) from Searles Lake, California. W. F. FOSHAG (*Amer. J. Sci.*, 1920, [iv], 49, 367—368).—Colourless, tabular, rhombohedral crystals were found embedded in powdery borax in a well boring at this locality. Material collected for analysis showed under the microscope some admixed halite. The following figures correspond with K_2SO_4 , 72.37; Na_2SO_4 , 18.38; NaCl, 7.87%, or $K_2SO_4:Na_2SO_4$ about 4:1.

K.	Na.	SO_4 .	Cl.	H_2O .	Total.
32.46	9.01	53.71	4.76	0.10	100.04
L. J. S.					

Analytical Chemistry.

Substitutes for Platinum Wire for Flame and Bead Tests. C. C. KIPLINGER (*J. Ind. Eng. Chem.*, 1920, 12, 500).—Borax beads may be made by heating the "lead" from a blacklead pencil to redness, dipping it into borax, and again placing it in the flame, so that a drop of the melted substance is suspended from the end. In using a roll of filter paper instead of platinum wire for flame tests (Ehringhaus, this vol., ii, 263), a flame of longer duration is produced, by introducing the rolled slip into a glass tube, with constricted opening, containing the solution or the substance moistened with hydrochloric acid. About 3 cm. of the paper is allowed to project, and the tube is inclined so as to feed the wick thus formed. C. A. M.

Thioacetic Acid as a Reagent. NAZARIO ALVAREZ (*Bol. minero soc. nac. min. Chile*, 1919, 31, 181—191).—Finely powdered phosphorus pentasulphide (300 grams) and glacial acetic acid (300 grams) are mixed in a 2-litre flask containing glass beads (150 grams) to prevent ignition, and the mixture is carefully heated to a temperature not exceeding 100° ; thioacetic acid begins to distil at 91° . Redistillation of the liquid serves to remove traces of arsenic and antimony. The ammonium salt is obtained by adding a slight excess of 10% ammonia to 10 c.c. of thioacetic acid. By diluting this solution to 30 c.c. a 33% solution of ammonium thioacetate is obtained, which, used in acid solution at 80 — 90° , has advantages (control of quantity, temperature, etc.) over hydrogen

sulphide for the precipitation of the bases of group II as sulphides; the filtrate, which contains ammonium chloride, is rendered available for the next group by boiling to remove hydrogen sulphide. The solution of ammonium thioacetate is not stable, and should be prepared when required for immediate use.

CHEMICAL ABSTRACTS.

Device for Preventing Over-titration. R. ORTHNER (*Chem. Zeit.*, 1920, **44**, 282—283).—A tube of about 5 mm. internal diameter, open at the top and constricted to a moderately fine jet at the lower end, is suspended vertically in the beaker containing the solution to be titrated; a short bent side-arm near the top of the tube is hooked over the edge of the beaker to keep the tube in position. The portion of the solution contained in this tube is not acted on by the reagent during the titration; the main portion of the solution is titrated until a very slight excess of reagent has been added; the tube is then raised so that its contents mix with the main portion of the solution, and the titration is completed.

W. P. S.

Colorimetric Determination of Titration Curves. LOUIS J. GILLESPIE (*J. Amer. Chem. Soc.*, 1920, **42**, 742—748).—A simple method is described for obtaining titration curves colorimetrically. The hydrogen ion exponents are determined without the use of buffer mixtures. Instead of a buffer mixture containing the indicator, a colour standard is used, consisting of a pair of test-tubes containing together 10 drops of indicator solution of suitable strength, the drop ratio in the two tubes being varied from 1:9 to 9:1. One tube of the pair contains dilute alkali and the other contains dilute acid. Reference to a table gives the hydrogen ion exponent corresponding with the drop ratio, or the exponent can be calculated from the relation $P_H = k + \log (\text{drop ratio})$, where the drop ratio is the ratio of the number of drops of the indicator solution in the alkali tube to that in the acid tube, and k is a constant depending on the indicator. It has the following values for the indicators named: tetrabromophenolsulphonaphthalein, 4.1; methyl-red, 5.0; dibromo-*o*-cresolsulphonaphthalein, 6.3; dibromothymolsulphonaphthalein, 7.1; phenolsulphonaphthalein, 7.7; *o*-cresolsulphonaphthalein, 8.1; and thymolsulphonaphthalein, 8.8.

J. F. S.

Potassium Hydrogen Phthalate as a Standard in Volumetric Analysis. W. S. HENDRIXSON (*J. Amer. Chem. Soc.*, 1920, **42**, 724—727. Compare A., 1915, ii, 797).—Potassium hydrogen phthalate is shown to be an excellent standard for volumetric work. It is best prepared from phthalic anhydride and potassium carbonate, and is obtained absolutely pure by three crystallisations. It contains no water of crystallisation, and is not hygroscopic, so that weighings may be made in open vessels. Its solubility has been determined in water, and the following values

obtained: 25°, 10.23%; 35°, 12.67%; and at the boiling point of the saturated solution, 36.12%.

J. F. S.

Automatic Methods of Gas Analysis depending on Thermal Conductivity. E. R. WEAVER, P. E. PALMER, H. W. FRANTZ, P. G. LEDIG, and S. F. PICKERING (*J. Ind. Eng. Chem.*, 1920, 12, 359—366).—An apparatus is described for the continuous analysis of gas mixtures by an electrical method depending on the thermal conductivity of the gas as compared with that of a standard gas or mixture. The apparatus is given in detail, and it may be adapted to record results automatically.

W. P. S.

New Forms of Combustion Apparatus for Use in Gas Analysis. E. R. WEAVER and P. G. LEDIG (*J. Ind. Eng. Chem.*, 1920, 12, 368—370).—A combustion pipette, of about 150 c.c. capacity, is provided with two short side-tubes, the outer ends of which are fitted with glass caps. These caps are cemented on and have short platinum leads passing through them, the inner ends of the leads connecting with a platinum spiral extending across the pipette from one side-tube to the other. A combustion capillary is also described; the igniting spiral of platinum wire extends vertically down a portion of the capillary between two short side-arms fitted with caps carrying the leads. This portion of the capillary is surrounded by a small water-jacket.

W. P. S.

Estimation of Chlorine with the Nephelometer. ARTHUR B. LAMB, PAUL W. CARLETON, and W. B. MELDRUM (*J. Amer. Chem. Soc.*, 1920, 42, 251—259).—The conditions to be observed in estimating traces of chlorine in alcohol and acetic acid solutions, by means of the nephelometer, have been investigated. It is shown that in a 50% alcohol water solution, heating silver chloride suspensions of widely differing concentrations at 40° for thirty minutes after precipitation produces a more intense and constant opalescence than can be attained at ordinary temperatures; further heating for thirty minutes at 40°, or keeping at the ordinary temperature for an hour, produces no perceptible change in this opalescence. Using this treatment, chlorides in such solutions may be estimated with an average deviation of 3—4% over concentrations ranging between 4 and 300×10^{-6} N. Opalescence in such solutions decays more rapidly in diffuse daylight than in the dark. The opalescence of the same quantity of silver chloride in water is about 15% greater than in 50% alcohol or in 50% acetic acid.

J. F. S.

Carbonyl Chloride. I. Detection and Estimation of Free Chlorine in Carbonyl Chloride. MARCEL DELÉPINE (*Bull. Soc. chim.*, 1920, [iv], 27, 283—286).—For the detection and estimation of free chlorine in carbonyl chloride by means of potassium iodide solution the concentration of the latter must not exceed 0.1%. After leading a known weight of the vapour of the carbonyl chloride into the potassium iodide solution, the free iodine is

titrated by means of standard thiosulphate. If the concentration of the potassium iodide solution exceeds 0.1% there is a risk of interaction between the iodide and the oxychloride with consequent liberation of iodine. W. G.

Carbonyl Chloride. II. Destruction of Carbonyl Chloride by Water; Estimation of Escaped Gases. M. DELÉPINE, R. DOURIS, and L. VILLE (*Bull. Soc. chim.*, 1920, [iv], 27, 286—288).—Carbonyl chloride is only slowly decomposed by moisture in the air, but is rapidly decomposed by water, although in the latter case the presence of hydrochloric acid considerably retards the decomposition. For the estimation of traces of carbonyl chloride in the air, a known volume of the air is bubbled through 10 c.c. of a solution containing 1 c.c. of *N*-sodium hydroxide and 5 c.c. of 95% alcohol, the volume being made up with water. The liquid is then evaporated to 2 c.c. on a water-bath, 2 drops of acetic acid are added, and the whole is evaporated to dryness; the residue is taken up with 2 c.c. of water, again evaporated to dryness, and once more taken up with 2 c.c. of water and the chloride present titrated with *N*/40-silver nitrate. By this means it is possible to estimate the chlorine to 0.00005 gram. W. G.

Carbonyl Chloride. V. Estimation of Hydrogen Chloride in Carbonyl Chloride. M. DELÉPINE, M. MONNOT, H. DUVAL, and J. LAFORE (*Bull. Soc. chim.*, 1920, [iv], 27, 292—295).—Five grams of finely powdered dry mercury cyanide are placed in a perfectly dry flask fitted with a ground-in stopper carrying two tubes. The carbonyl chloride is introduced into the flask in a sealed bulb, and the flask is exhausted. The bulb is then broken, and after twelve to fourteen hours the hydrogen cyanide formed by the action of any hydrogen chloride in the carbonyl chloride on the mercury cyanide is aspirated off and collected in 50 c.c. of 2*N*-sodium hydroxide, and is then estimated by Denigès's method. W. G.

Some Factors influencing the Estimation of Chlorides in Soil. C. T. HIRST and J. E. GREAVES (*Soil Sci.*, 1920, 9, 41—51).—For the estimation of chlorides in soil the Volhard method gives more concordant and, as judged by the gravimetric method, more nearly exact results than the Mohr method. The following is the most satisfactory procedure to adopt. One hundred grams of finely powdered soil are shaken for five minutes with 500 c.c. of water and the solution is clarified either by the addition of 2 grams of alum or by filtration through a Pasteur-Chamberland filter. Twenty c.c. portions of the clear filtrate are transferred to stoppered bottles, and an excess of *N*/10-silver nitrate is added, followed by 10 c.c. of 95% alcohol. The mixture is shaken until the silver chloride is coagulated, after which 2 c.c. of a 4% ferric sulphate solution and 5 c.c. of dilute nitric acid are added, and the excess of silver nitrate is titrated with *N*/10-ammonium thiocyanate. W. G.

Estimation of Iodide and Bromide in Mineral Waters and Brines. W. F. BAUGHMAN and W. W. SKINNER (*J. Ind. Eng. Chem.*, 1920, **12**, 358).—Iodides are estimated by the permanganate method (A., 1919, ii, 349). Another portion of the sample is distilled with ferric sulphate to remove iodine, the distillation then treated with a slight excess of ammonia, boiled, filtered, the filtrate evaporated to dryness, and the bromine estimated in this residue by the chromic acid method (this vol., ii, 48). W. P. S.

Detection of Sulphuric Ions Masked in Complex Compounds. P. JOB and G. URBAIN (*Compt. rend.*, 1920, **170**, 843—845).—The $\text{SO}_4^{''}$ ion masked in complex cobalt compounds may be estimated by difference. The total $\text{SO}_4^{''}$ is estimated in the ordinary way as barium sulphate, and the free $\text{SO}_4^{''}$ is estimated by precipitation in the cold as benzidine sulphate. The difference between the two results gives the percentage of masked $\text{SO}_4^{''}$ ions in the complex. W. G.

Differentiation of Masked and Apparent Sulphuric Radicles in Complex Salts. ANDRÉ KLING and DANIEL FLORENTIN (*Compt. rend.*, 1920, **170**, 992—995. Compare A., 1914, ii, 661).—A claim for priority over Job and Urbain (compare preceding abstract) for the use of benzidine hydrochloride in the estimation of free sulphate ions in complex cobalt salts. W. G.

Solubility of Benzidine Sulphate in Water. C. S. BISSON and A. W. CHRISTIE (*J. Ind. Eng. Chem.*, 1920, **12**, 485—486).—The solubility of benzidine sulphate in water at various temperatures was determined by evaporating a measured quantity of the solution, and also by titration with potassium permanganate solution in the presence of sulphuric acid. The solubility increased from 0.049 gram per litre at 0° to 0.290 (and 0.252) at 80°. The solution obtained at 80° was discoloured, even after twenty-four hours in a thermostat. This was probably due to partial oxidation of the benzidine, and accounts for the discrepancy between the results obtained by the two methods. The residue obtained at 50° (0.141 and 0.149 gram per litre) was only slightly discoloured, and probably gives the approximate solubility at that temperature. The results show that the smallest possible amount of cold water should be used for washing benzidine sulphate in the quantitative estimation of sulphate. C. A. M.

Simplified Evaluation of Hyposulphite (Blankite; Redo). G. BRUNN (*Zeitsch. angew. Chem.*, 1920, **33**, 92).—The usual method of estimating hyposulphite by titrating a solution of the salt with potassium ferricyanide is subject to error on account of the rapidity with which the salt is oxidised in solution by atmospheric oxygen. The analysis can be carried out quickly and accurately in the following manner. In a porcelain dish are placed 20 c.c. of a standard potassium ferricyanide solution with a trace of ferrous sulphate sufficient to form a blue colloidal solution but not

a precipitate. A slight excess of the hyposulphite is weighed out in a scoop, and the salt is carefully dusted into the solution, with careful stirring, until the end-point, indicated by a change in colour from blue to bright reddish-yellow, is reached. The scoop is then weighed again to determine the weight of hyposulphite used. The accuracy of the method depends solely on the skill of the manipulator in dusting the powder into the solution. There is a small constant error due to the oxygen dissolved in the ferricyanide solution, but this is probably under 0.5%.
E. H. R.

Boric Acid Modification of the Kjeldahl Method for Crop and Soil Analysis. F. M. SCALES and A. P. HARRISON (*J. Ind. Eng. Chem.*, 1920, 12, 350—352).—The use of 4% boric acid solution as proposed by Winkler (A., 1913, ii, 527) for absorbing the ammonia in the distillation part of the Kjeldahl method is trustworthy. Bromophenol-blue is a suitable indicator for the subsequent titration.
W. P. S.

Method for Estimating Nitrogen in Sodium Nitrate by the Modified Devarda Method and the Use of the Davisson Scrubber Bulb. C. A. BURR (*J. Ind. Eng. Chem.*, 1920, 12, 352, 354).—The reduction process described by E. R. Allen (A., 1915, ii, 575) is recommended, the scrubber bulb designed by Davisson (A., 1919, ii, 296) being used to prevent alkali spray passing into the receiver.
W. P. S.

Estimation of Nitrogen in Calcium Nitrate. E. PLATOU (*Chim. et Ind.*, 1920, 3, 310—312).—As manufactured in the Pyrenees by neutralising synthetic nitric acid with limestone, calcium nitrate contains on the average 76.15% of calcium nitrate and 21.45% of water, with small amounts (0.1—0.55%) of other salts of calcium, magnesium, iron, and aluminium. As the material is hygroscopic a fairly large sample (10 to 25 grams) should be dissolved, and portions of the solution taken. The most trustworthy method of estimating the nitrogen is to reduce it in alkaline solution by means of Devarda's alloy, and to distil the ammonia. [See also *J. Soc. Chem. Ind.*, 1920, 401A.]
C. A. M.

Estimation of Ammonia in Cultures in Presence of Urea. PIERRE THOMAS (*Bull. Soc. chim. biol.*, 1919, 1, 171—175).—To 50 or 100 c.c. of the liquid are added several drops of pure hydrochloric acid and 10% solution of lead acetate until no further precipitation occurs. A little finely powdered lead carbonate is then added, and the whole left for fifteen or eighteen hours. After filtration and washing with cold water, all the ammonia will be found in the filtrate, and the interference of phosphates will be prevented by the preliminary precipitation. The filtrate is introduced into a special form of apparatus, which is illustrated, and 5 grams of magnesium carbonate added. Ammonia is driven off by vacuum distillation below 40°, and is estimated by absorption in standard acid.
J. C. D.

Carbonyl Chloride. IV. Estimation of Carbonyl Chloride in Titanium Chloride. M. DELÉPINE and J. LAFORE (*Bull. Soc. chim.*, 1920, [iv], **27**, 290—292).—The method is based on the measurement of the carbon dioxide liberated when the carbonyl chloride is decomposed by water. A special apparatus is described, designed to overcome the difficulty due to the formation of plugs of oxide or oxychloride of titanium at the end of the inlet tube for the sample of titanium chloride. The carbon dioxide is aspirated off, collected in barium hydroxide, and estimated volumetrically. W. G.

Hydrolytic Decomposition of Alkali Aluminates and Methods of Determining the Concentration of Hydroxyl Ions in Concentrated Solutions of Alkali Hydroxides.

ROBERT FRICKE (*Zeitsch. Elektrochem.*, 1920, **26**, 129—151).—After a long account of the literature of the hydrolysis of alkali aluminates an account is given of an investigation of the so-called "crystalline" alumina obtained from solutions of the alkali aluminates and of the solutions in equilibrium with the precipitated alumina. Two methods are described whereby, from potential measurements of elements of the type $\text{Hg}|\text{Hg}_2\text{Cl}_2||\text{sat. KCl}||\text{alkaline solution}|\text{PtH}$, an approximate measure of the hydroxyl-ion concentration of highly concentrated solutions of alkali hydroxide may be obtained. By this means it is shown that considerable difference occurs between the hydroxyl-ion concentration of sodium and potassium hydroxides in concentrated solutions. By means of titration experiments it is shown that the hydrolysis of alkali aluminates is a time reaction. The so-called crystalline alumina is not crystalline and possesses properties which vary with the age of the preparation. The ageing of alumina is proportional to the hydroxyl-ion concentration of the alkali solution in equilibrium with it. Measurements on the viscosity of solutions of alkali aluminates indicate that the sodium hydroxide molecule (or the sodium ion) is probably more strongly hydrated than the potassium hydroxide molecule (or the potassium ion). Freezing-point measurements and potential measurements show that aged solutions of aluminates contain considerable quantities of colloidal alumina. J. F. S.

Potassium Chlorate as a Standardising Substance for Solutions of Alkali. H. B. VAN VALKENBURGH (*J. Amer. Chem. Soc.*, 1920, **42**, 757—760).—Potassium chlorate may be used as a standard in titrating alkali by the following method. The chlorate is dried at 240° for four to six hours, the solution is boiled in an Erlenmeyer flask, sulphur dioxide passed in for thirty minutes, and the boiling continued for a further ten minutes to remove all excess of sulphur dioxide. Phenolphthalein is then added, and the solution titrated either hot or cold with alkali. The calculation of the strength of the alkali is based on the equation $\text{KClO}_3 + 3\text{SO}_2 + 3\text{H}_2\text{O} = 3\text{H}_2\text{SO}_4 + \text{KCl}$. The results of titrations by this method agree with those obtained by titrating the alkali with standard acid. J. F. S.

Estimation of Potassium as Perchlorate. II. GREGORY P. BAXTER and MATSUSUKE KOBAYASHI (*J. Amer. Chem. Soc.*, 1920, **42**, 735—742. Compare A., 1917, ii, 270).—The method of estimating potassium by the perchlorate method has, as a result of the publication of Gooch and Blake (A., 1918, ii, 20), been further investigated. The authors maintain the efficiency of the method previously published, with the modification that the initial extraction of the sodium perchlorate should be carried out with alcohol containing perchloric acid, but not potassium perchlorate, instead of with a saturated solution of the latter salt. When the quantity of sodium is small, the use of a saturated solution of potassium perchlorate for the initial washing is safe, but when the quantity of sodium is large, the potassium salt is best washed once or twice with alcohol containing perchloric acid before the use of the saturated solution of the precipitate is commenced. The chief points to be observed in the estimation are: (i) the use of absolute alcohol; (ii) a low temperature (0° if possible); (iii) filtration in a platinum-sponge crucible; (iv) at least one solution of the precipitate in water and re-evaporation to dryness in the course of the washing; (v) the use of alcohol containing perchloric acid and saturated with potassium perchlorate at the temperature of washing, for washing the precipitate after the sodium salt has been removed by washing with alcohol containing perchloric acid. Using this method, the error is never more than a few tenths of a milligram. J. F. S.

Iodic Acid a Microchemical Reagent for Soluble and Insoluble Compounds of Calcium, Strontium, or Barium. G. DENIGÈS (*Compt. rend.*, 1920, **170**, 996—998).—Iodic acid, in 10% aqueous solution, gives almost immediately finely crystalline, characteristic precipitates of calcium, strontium, or barium iodate with salts of these metals. This serves as a basis for the microchemical detection of these metals. An insoluble salt is finely powdered and suspended in a drop of water on a microscope slide, and a drop of the iodic acid solution is added, the formation of the crystalline precipitate being observed under the microscope. A soluble salt is dissolved in water, one drop of the solution being used. If barium is present as the sulphate, this salt is best reduced by heating it on a platinum wire in a reducing flame, the test being applied to the resulting sulphide. Calcium iodate or periodate should be first ignited to the iodide before applying the test. W. G.

The Spectrographic Detection of Metals and Specially of Zinc in the Animal Organism. A. DE GRAMONT (*Compt. rend.*, 1920, **170**, 1037—1039).—Using the method of spectral analysis previously employed for the detection of titanium (compare A., 1918, ii, 49), zinc may readily be detected in the ash from cobra venom by its rays $\lambda=4811$ and 4722 and the ultra-violet ray $\lambda=3345$. The method is also suitable for the detection of traces of iron. W. G.

Rapid Estimation of Copper in Copper-Aluminium Alloys. PIERRE HULOT (*Ann. Chim. anal.*, 1920, [ii], 2, 103).—A portion of the finely divided alloy is treated with 20% potassium hydroxide solution, which dissolves the aluminium. The insoluble residue of copper is then collected, washed, and weighed, or dissolved in nitric acid, converted into sulphate, and estimated electrolytically.

W. P. S.

Detection of Manganese and Zinc in the Presence of Phosphates or Oxalates. E. SCHMIDT (*Ber. deut. Pharm. Ges.*, 1920, 30, 217—218). Manganese and zinc are precipitated together by means of ammonium sulphide, and are then separated by a method based on the different solubilities of their respective hydroxides, $Mn(OH)_2$ and $Zn(OH)_2$, in a solution of ammonia and ammonium chloride. Wester's statement (this vol., ii, 334) that in the presence of phosphoric or oxalic acid the metals are precipitated as phosphates or oxalates is incorrect, since the precipitates consist of sulphides even under these conditions. This is shown by the fact that on treating a solution of manganese sulphate containing ammonium chloride with ammoniacal ammonium sodium phosphate solution in excess, and then saturating the liquid with hydrogen sulphide, the precipitated manganese phosphate is converted into manganese sulphide. An addition of ammonium sulphide does not effect this conversion under these conditions.

C. A. M.

Estimation of Iron in Iron Ores by means of Permanganate. R. SCHWARZ (*Chem. Zeit.*, 1920, 44, 310—311).—In reply to the criticisms of Brandt (this vol., ii, 269) on the method of Schwarz and Rolfes (*A.*, 1919, ii, 170), experiments are described which show that colloidal silicic acid solutions have no disturbing influence on the results of the titration of iron in sulphuric acid solution. On the contrary, the sol in association with the manganous salt has a favourable influence on the titration of iron in hydrochloric acid solution. There is no evidence of the alleged formation of an intermediate persilicic acid.

C. A. M.

Method for the Analysis of an Iron Ore. ERNEST LITTLE and WILLARD L. HULT (*J. Ind. Eng. Chem.*, 1920, 12, 269—273).—The ore is dissolved in hydrochloric acid, the ferric salts are reduced, and the solution is diluted and treated with an excess of standardised potassium dichromate solution. Five grams of ammonium fluoride and 5 grams of potassium iodide are then added, and the iodine liberated by the excess of dichromate is titrated with thiosulphate solution. The ammonium fluoride prevents the action of the ferric salts on the iodide. The preliminary reduction of the ferric salts may be made with stannous chloride solution (avoiding an excess), mercuric chloride being added afterwards, but the use of the Jones' reductor is recommended.

W. P. S.

Use of Cupferron in Quantitative Analysis. G. E. F. LUNDELL and H. B. KNOWLES (*J. Ind. Eng. Chem.*, 1920, **12**, 344—350).—Cupferron (the ammonium salt of nitrosophenylhydroxylamine) has been used for the separation of iron from manganese, and iron and titanium from aluminium and manganese; its use has also been found trustworthy for the estimation of iron, copper, titanium, zirconium, thorium, and vanadium. In most cases, however, the "cupferron" method does not offer any advantages over ordinary established methods. The following substances interfere with the separations: silver, mercury, tin, lead, bismuth, cerium, tungsten, uranium, silica, and excessive amounts of phosphorus, alkalis, and alkaline earths. W. P. S.

Influence of Atmospheric Oxygen on the Iodometric Estimation of Chromium. OTTO MEINDL (*Zeitsch. anal. Chem.*, 1919, **58**, 529—548).—The iodometric estimation of chromium is affected by atmospheric oxygen, since the latter enters into the reaction between the chromic acid and hydriodic acid. The results obtained are too high, the error increasing with the time of contact. W. P. S.

A Test for Molybdenite. F. C. FUCHS (*Informaciones y mem. soc. ing. Peru*, 1918, **20**, 423).—The mineral to be tested is dissolved in fused potassium hydroxide. If molybdenum sulphide is present, it dissolves with an intense red colour. If the fused mass is cooled and dissolved in water, the colour changes to blue, green, yellow, etc., corresponding with the various states of combination of molybdenum. The reaction is explicable on the theory that molybdenum sulphide gives up one of its sulphur atoms to the fused potassium hydroxide, forming a red, double sulphide.

CHEMICAL ABSTRACTS.

Estimation of Tungsten. R. F. HEATH (*Chem. Trade J.*, 1920, **66**, 629).—The sample is fused with sodium peroxide, and the filtered extract of the mass treated with 6—7 c.c. of a solution prepared by dissolving 10.3 grams of stannous and 2.1 grams of stannic chlorides in 100 c.c. of dilute acetic and 40 c.c. of syrupy phosphoric acids. Three to four c.c. of sulphuric acid are added, and, after allowing the blue colour to develop for several minutes, it is compared with that produced by the reagent in solutions of known tungsten content. [See also *J. Soc. Chem. Ind.*, 1920, June.] A. R. P.

Analysis of Tungsten. JOSEPH ERLICH (*Ann. Chim. anal.*, 1920, [ii], **2**, 102—103).—The tungsten is heated with hydrochloric acid and ferric chloride, and the insoluble portion is collected, washed with ammonium nitrate solution, ignited, and weighed. The ignited residue is then fused with sodium hydrogen sulphate, dissolved in ammonia, and the solution treated with ammonium carbonate; the tungstic oxide remains in solution, and

the impurities, which are precipitated, are collected, ignited, weighed, and their weight deducted from the weight first obtained. The difference between the two weights gives the quantity of tungstic oxide present. Two fusions with sodium hydrogen sulphate may be necessary in order to separate all the impurities.

W. P. S.

Estimation of Tungstic Acid in Tungsten Concentrates.

HÉRCULES CORTI (*Anal. Soc. Quim. Argentina*, 1917, 5, 308—326).—A detailed description is given of the estimation of tungstic acid in wolfram or scheelite concentrates by decomposing the finely powdered ore with hydrochloric acid, evaporating to dryness to render silica insoluble, dissolving the tungstic acid in the washed residue with ammonia, evaporating the filtrate, and igniting the residual WO_3 . [See *J. Soc. Chem. Ind.*, 1920, June.]

W. R. S.

The Salts of Nitrosophenylhydroxylamine (Cupferron) ; Uranous Salt.

V. AUGER (*Compt. rend.*, 1920, 170, 995—996).—In neutral solution, cupferron gives precipitates with all the metallic salts except those of the alkali metals, the precipitates obtained being divisible into simple salts, insoluble in chloroform and decomposed by dilute acids, and complex salts, soluble in chloroform and more or less resistant to concentrated acids.

Uranyl salts do not give precipitates with cupferron, but if they are first reduced by zinc to uranous salt, then the whole of the uranium is precipitated in acid solution by cupferron. The uranous salt obtained is soluble in chloroform, from which it crystallises in brown prisms, $(\text{C}_6\text{H}_5\text{O}_2\text{N}_2)_4\text{U}$. Thus, by this means, vanadium and uranium may be separated by successive precipitation.

W. G.

The Estimation of Uranium.

R. SCHWARZ (*Helv. Chim. Acta*, 1920, 3, 330—346).—Of the various precipitants recommended for uranium, mercuric oxide is untrustworthy, hydrogen peroxide is quite unsatisfactory, ethylenediamine has no advantages over ammonia, and hydrofluoric and oxalic acids are inconvenient. The simplest and most trustworthy agents are ammonium sulphide and ammonia. Precipitation with the former is best carried out at 80° in presence of ammonium chloride; some ammonium uranate is always formed, and, further, complete separation from the alkali metals is only attained by repeating the precipitation. Precipitation with ammonia should be performed at 100° in presence of ammonium chloride, and preferably not in glass vessels, owing to the tendency of ammonium uranate to carry silica with it. Ignition of the precipitate from either process to uranosouranic oxide (Zimmermann, A., 1886, 598) is best carried out in porcelain crucibles with access of air, since platinum permits diffusion of gases from the flame, and consequent reduction. Its reduction by means of hydrogen to uranous oxide is not quanti-

tative (Kern, A., 1902, ii, 51), owing to the formation of nitride. The separation of uranium from the alkali metals in the form of uranyl phosphate (Kern) was found to be almost impossible owing to the fineness of the precipitate obtained. Of volumetric processes, that involving the solution of uranosouranic oxide in sulphuric acid (Boller, *Diss.*, Zurich, 1915) was simplified and gave good results; this was not the case, however, if complete reduction to urano-salts were first attempted (compare Pulmann, A., 1903, ii, 761). The estimation of uranium in presence of aluminium is most conveniently performed titrimetrically. The precipitation of aluminium by means of ammonium carbonate in presence of ammonium salts is incomplete, and some uranium is also carried down; a complicated procedure, which, however, gives good results, is necessary to effect complete separation. Contrary to Kern's view, Pisani's process (1861) for the separation of iron from uranium by ammonium carbonate and ammonium sulphide is quite effective. Ditte's process (this Journ., 1877, ii, 926) for the separation from chromium salts is unsatisfactory (compare Formánek, A., 1890, 852), and they must first be oxidised to chromate, most suitably by alkaline hypobromite, although Jannasch's ammonium persulphate method gives exact results. Sodium uranate, when precipitated in presence of chromate (Gibbs, this Journ., 1874, 93), always contains uranyl alkali chromates, and the precipitation must therefore be repeated; it is also advisable to redissolve the uranosouranic oxide finally obtained in nitric acid to separate it from silica.

A redetermination of the dissociation tension of uranosouranic oxide gave results differing from those of Colani (A., 1907, ii, 878), and, taken in conjunction with the heat of formation of uranosouranic oxide from uranous oxide (Mixer, A., 1912, ii, 899), indicate the existence of an intermediate oxide. Further, by igniting the higher oxide in a stream of carbon dioxide in an electric furnace at 1122°, a black residue was obtained corresponding approximately in composition with the formula U_2O_5 ; traces of nitride were produced when nitrogen was employed. The contrary results of Zimmermann (*loc. cit.*) were vitiated by his use of a platinum crucible over a gas flame, which permitted reduction. For the same reason, the ignition of chromic oxide is best carried out in a platinum crucible, since this avoids the formation of chromichromate otherwise observed (Rothang, A., 1914, ii, 73). J. K.

Estimation of Nitroform by Potassium Permanganate.
PHYLLIS VIOLET McKIE (T., 1920, 117, 646—648).

Reactions of Chloropicrin. GUILLEMAUD and LABAT (*Bull. Soc. pharm., Bordeaux*, 1919; from *Ann. Chim. anal.*, 1920, [ii], 2, 120—121).—The odour of chloropicrin is destroyed by alkali polysulphide solution. When a drop of chloropicrin is boiled with alcoholic potassium hydroxide solution and a small quantity of thymol, a yellow coloration is obtained; if the thymol is replaced by resorcinol, the coloration is red. The addition of sulphuric acid

to the alkaline thymol mixture produces a reddish-violet coloration, and the whole mixture, on dilution with acetic acid, exhibits an absorption band in the green portion of the spectrum. Chloroform yields slightly different colorations under the above conditions, but a mixture of chloroform and a trace of sodium nitrite yields the same reactions as does chloropicrin. Both chloroform and chloropicrin yield a carbylamine. When chloropicrin is boiled with potassium hydroxide solution, the mixture, after cooling, yields reactions characteristic of nitrous acid.

W. P. S.

Estimation of Methyl Alcohol. S. B. SCHRYVER and CYRIL CHRISTIAN WOOD (*Analyst*, 1920, **45**, 164—170).—A method for the estimation of methyl alcohol in aqueous solution is described, the essential principle of the method being the determination of the concentration of ammonium persulphate necessary to destroy completely the formaldehyde formed in the initial stages of the oxidation process under certain specified conditions of experiment. The formaldehyde is detected by the phenylhydrazine hydrochloride and potassium ferrieyanide test described previously by one of the authors (Schryver, A., 1910, ii, 335). By slight modification, the method may be used for the estimation of methyl alcohol in acetone. To estimate methyl alcohol in ethyl alcohol, the mixture of alcohols is oxidised partly by a relatively small amount of persulphate (the alcohols being in excess), and the formaldehyde formed is estimated colorimetrically. [See, further, *J. Soc. Chem. Ind.*, 1920, June.]

W. P. S.

Use of Diastatic Reagents in Analytical Investigations. Differentiation between Guaiacol and Creosote. LUCIANO P. J. PALET (*Anal. Soc. Quím. Argentina*, 1917, **5**, 305—307).—Creosote is known to have been used as a substitute for guaiacol in medicinal preparations. They may be differentiated by dissolving the residue from the chloroform extract of the sample in alcohol and adding a direct oxydase. In presence of guaiacol, a yellow coloration is obtained at once, which gradually turns orange. Creosote under the same conditions gives no colour; after more than half an hour, a slight violet tint develops. If a few drops of hydrogen peroxide are also added to the test, guaiacol gives a more intense colour, whilst creosote furnishes a strong, reddish-violet coloration; indirect oxydases may be used when hydrogen peroxide is added. It is recommended to carry out the reactions in dilute solution.

W. R. S.

The Systematic Detection of Acetates. L. J. CURTMAN, D. A. BROGGI, and V. FOURMAN (*Chem. News*, 1920, **120**, 230).—To detect acetates in mixtures, the following procedure is recommended. The solution is acidified with 10% nitric acid and 5 c.c. in excess added, followed by *N*/4-silver nitrate until no further precipitate is formed. After filtering, the clear liquid is made just alkaline with sodium hydroxide, and 10 c.c. each of 2*N*-barium chloride

and 2*N*-calcium chloride solutions added. The precipitate is filtered off, and the filtrate evaporated to 5 c.c. after addition of 10 c.c. of 3% hydrogen peroxide. The crystals are filtered off, and the filtrate made just neutral to phenolphthalein with hydrochloric acid. One c.c. of *N*/2-ferric chloride solution is added, and the colour compared against that of 1 c.c. of the reagent in 5 c.c. of water. Two mg. of acetic acid give a pale reddish-yellow colour. The odour of acetic acid is perceptible if 1 c.c. of a solution containing at least 2 mg. of the acid is boiled with 2 c.c. of 1:1 sulphuric acid, but nitrates seriously interfere with the test.

A. R. P.

Estimation of the Total Non-amino-organic Acids in Urine. A. DESGREZ and M. POLONOWSKI (*Compt. rend.*, 1920, 170, 1008—1010).—One hundred c.c. of the urine are made alkaline with sodium carbonate and evaporated to dryness on a water-bath. The residue is mixed with pure sand moistened with a slight excess of phosphoric acid, and the whole is extracted with ether containing 1% of alcohol in a Louise apparatus for ten hours. To the ethereal extract a known volume of *N*-sodium hydroxide is added, and the excess is titrated with *N*-sulphuric acid.

To obtain some idea of the molecular weight of the non-amino-acids and to correct for any hydrochloric acid present, the ethereal extract is shaken several times with a solution of barium hydroxide. The insoluble barium salts are collected, washed, dried at 110°, weighed, ignited to barium carbonate, and weighed again. These two weighings give a means of calculating the average molecular weights of the barium salts insoluble in water. The filtrate from the above precipitate is freed from excess of barium by carbon dioxide, and the solution is filtered, evaporated to dryness, and the residue weighed. By calcination, the organic barium salts are converted into carbonates, and the residue is again weighed. The carbonate is converted into chloride, and the total chloride is dried and weighed. The three weighings allow of a calculation of the amount of chloride mixed with the organic salts, the total weight of the latter, and their average molecular weight.

W. G.

A New Reaction of Acetaldehyde. LUCAS TSALAPATANIS (*Anal. Soc. Quim. Argentina*, 1917, 5, 244—245).—The liquid to be tested is heated with 1–2 c.c. of an aqueous solution of resorcinol and a few drops of 10% sodium hydroxide solution. After two minutes, a bluish-green coloration appears in dilute, and a red one in concentrated, solutions. The reaction is extremely sensitive. The colour, which is very stable, is destroyed by acids, but restored by sodium hydroxide.

W. R. S.

Microchemical Method for the Estimation of Sugar in Body Fluids. R. GOIFFON and F. NERVEUX (*Compt. rend. Soc. Biol.*, 1920, 83, 121; from *J. Pharm. Chim.*, 1920, [vii], 21, 357—359).—A portion of the fluid, after suitable clarification, is boiled with Fehling's solution, the cuprous oxide is collected,

washed, dissolved in a minimum quantity of hydrochloric acid, a few drops of potassium ferrocyanide solution and three drops of saturated tartaric acid solution are added, and the coloration obtained is compared with those shown by standards prepared under similar conditions from known amounts of sugar.

W. P. S.

The Iodometric Estimation of Sugars. HILDA MARY JUDD (*Biochem. J.*, 1920, **14**, 255—261).—Estimation of levulose in fruit juices by the polarimetric method is untrustworthy. Various iodometric methods for the estimation of aldoses in the presence of ketoses have been tested, and none of them was found to give quantitative results. This is ascribed to the action of the dilute alkalis on the sugars. In using either the method of Colin and Lievin (A., 1918, ii, 461), or that of Willstätter and Schudel (A., 1918, ii, 337), a definite and constant weight of iodine always reacts with a given weight of dextrose. This weight of iodine is not affected by the changes in the amount of alkali present, or by the presence of other sugars. This is also true of levulose. It is therefore possible to calculate the amount of dextrose and levulose in a solution from the copper-reducing power and the iodine figure. Each sugar has its own characteristic iodine value. Rhamnose behaves very abnormally. Sucrose is not oxidised, whilst lactose and maltose are both oxidised, the former requiring twice as much iodine as the latter.

J. C. D.

Estimation of Sugars by Inversion. E. HILDT (*Ann. Chim. anal.*, 1920, [ii], **2**, 103—106).—A discussion regarding methods for the inversion of sugars. Chemical catalysts possess advantages over enzymes, since they have a definite action under given conditions. Certain aromatic sulphonic acids (benzenesulphonic acid, etc.) are particularly useful for this purpose, especially in the estimation of sugars in sweetened condensed milk.

W. P. S.

A Cryoscopic Method for the Estimation of Sucrose. HENRY H. DIXON and T. G. MASON (*Sci. Proc. Roy. Dubl. Soc.*, 1920, **16**, 1—8).—The method consists in determining the freezing point of the solution before and after the inversion of the sucrose by invertase. The freezing point is determined by the thermoelectric method described by Dixon (compare A., 1911, ii, 853). In the case of plant sap, the tissues are frozen and the sap pressed out. The sap is boiled and filtered, and weighed quantities are cooled in test-tubes to -2° . The requisite amount (0.33 gram) of invertase is added and the freezing point determined. The mixture is then incubated at 28° for twenty-four hours and the freezing point again determined. The increase in the depression of the freezing point is a measure of the sucrose originally present. A preliminary removal of gums, etc., from the sap is not necessary. Using 2.5 c.c. of sap the probable error is 0.0016 gram of sucrose.

W. G.

Estimation of Amino-acids by means of the H₂drogen Electrode. E. L. TAGUE (*J. Amer. Chem. Soc.*, 1920, **42**, 174—184).—Neutralisation curves have been obtained for the amino-acids, lysine dihydrochloride, glutamic acid, tyrosine, phenyl-alanine and glycine. The method consists in adding standard alkali hydroxide solution to a definite volume of an aqueous solution of the acid and measuring the hydrogen-ion concentration after each addition; this process is continued until the solution has a P_H value of 12.5. Then to an equal volume of water, proceeding in the same way, the same standard alkali is added until the same P_H value is obtained, care being taken to add sufficient water to give the blank the same volume as that of the original solution at the P_H value. Subtracting the number of c.c. used in the blank from that required in the original titration gives the number of c.c. of standard alkali necessary to neutralise the amino-acid alone. In this way it is possible to obtain the neutralisation curves of the amino-acids alone, and the influence of the different groups may be seen. Certain inaccuracies in the formalin titration method are explained by this method. An hydroxyl-ion concentration of about 2×10^{-2} ($P_H=12.5$) will suppress the basic ionisation of the sodium salts of the amino-acids to a negligible extent, and thus make it possible to obtain a more exact quantitative estimation of the diamino-acids as well as of others containing strongly negative groups. J. F. S.

Method of Graduating Ureometers of the Yvon Type. CH. O. GUILLAUMIN (*J. Pharm. Chim.*, 1920, [vii], **21**, 342—346).—The ureometer is supported vertically with the tap at the lower end, and is filled with water; the open end is closed by a rubber stopper through which passes the end of a very narrow, graduated tube about 18 cm. long and having a capacity of 2 c.c. The ureometer is then turned so that the tap is at the top, the level of the water having been adjusted previously to the zero mark on the graduated tube, and small quantities of air are admitted successively through the tap, the volumes of these quantities being given by the changes in level of the water in the graduated tube. W. P. S.

Braunstein's Modification of the Mörner-Sjöqvist Process for the Estimation of Urea. ALAN HERZPATH TODD (*Biochem. J.*, 1920, **14**, 252—254).—This modification (A., 1901, ii, 140) does not give a quantitative yield of urea nitrogen. Ignition of the filtrate for fourteen hours at 185° with 15 grams of crystalline phosphoric acid gives an accurate result. J. C. D.

Estimation of Uric Acid by a Modification of Blarez and Tourrou's Method. G. PÉGURIER (*Ann. Chim. anal.*, 1920, [ii], **2**, 109—110).—Fifty c.c. of urine are treated with 5 c.c. of saturated sodium carbonate solution, and the mixture is added

...hling's solution decolorised previously by the sodium hydrogen sulphite solution. The precipitate collected on a filter, and washed with water; the precipitate are then transferred to a beaker containing 10 c.c. of water and 10 c.c. of dilute sulphuric acid (1:1), and the mixture is titrated with 0.212% potassium permanganate solution. Each c.c. of the latter corresponds with 0.1 gram of uric acid per c.c. of urine.

W. P. S.

Action of the Arsenotungstic Reagent on certain Alkaloids and Glucosides. LUCIANO P. J. PALET (*Anal. Soc. Quim. Argentina*, 1916, 4, 256—258).—The arsenotungstic reagent for phenolic groups proposed by Guglielmelli (A., 1916, ii, 584) has been applied to a large number of alkaloids and glucosides, and the result is tabulated in the original.

W. R. S.

Forensic Investigation of Aconitine. Its Resistance to Putrefaction. LUCIANO P. J. PALET (*Anal. Soc. Quim. Argentina*, 1918, 6, 480—487).—A rat was killed by subcutaneous injection of 0.002 gram of aconitine. The carcase was left to putrefy seven days in the air, and subsequently buried during two months in a metal box. The pulped viscera were treated with absolute alcohol, slightly acidified with 10% tartaric acid, and kept for fifteen minutes at 50°; the cooled liquid was filtered and distilled in a vacuum; the residue was left overnight in contact with 250 c.c. of absolute alcohol, the liquid filtered, and distilled in a vacuum. This treatment was repeated twice. The final residue was dissolved with 200 c.c. of water, which was distilled off to remove alcohol, again dissolved in water, and filtered. This liquid was extracted in a separator (1) with ether, (2) with ether after previous addition of sodium hydrogen carbonate to feebly alkaline reaction, and (3) with chloroform. The last extract was evaporated and the residue treated with 10% acetic acid. It gave positive reactions with Mayer's and Monti's reagents, had the characteristic action on the tongue, and gave a violet coloration with a solution of 1 gram of sodium molybdate in 25 grams of phosphoric acid. Brouardel and Boutmy's reaction for ptomaine was negative. The conclusions are: that aconitine is not destroyed by the natural blood ferments; that it resists putrefaction for two months; that weak acids and alkalis should be used for its extraction; that its characterisation may be effected by the organoleptic test and the reaction with phosphoric acid and sodium molybdate; that crystallised aconitine does not give a violet coloration with official phosphoric acid, either hot or cold.

W. R. S.

Test for Strychnine. H. E. BUC (*J. Assoc. Off. Agric. Chem.*, 1919, 3, 193).—One gram of zinc amalgam and 0.5 c.c. of hydrochloric acid are added to 0.5 c.c. of the strychnine salt solution; after fifteen minutes, the liquid is decanted and treated, drop by drop, with 0.02% potassium ferricyanide solution. A pink to rose-red coloration is obtained. The zinc amalgam is prepared by

washing granulated zinc with hydrochloric acid for one hour with 1% potassium antimonyl tartrate solution, then with mercuric chloride solution and a small amount of acetic acid; after thirty minutes, the zinc is removed, washed, and dried. The test will detect the presence of other alkaloids and certain organic substances.

Use of Ethyl Acetate as a Precipitating Reagent for Proteins.

A. MARIE (*Ann. Inst. Pasteur*, 1920, **34**, 159—161).—Ethyl acetate gives a marked precipitate with even dilute solutions of proteins, and a turbidity with peptones, proteoses, or albumoses, but solutions of amino-acids or vegetable or animal alkaloids show no apparent change in their physical state on its addition.

W. G.

Important Source of Error in Investigating Urines for Albumin by means of Sulphosalicylic Acid. SCHALL (*Münch. med. Woch.*, 1920, **67**, 164—165; from *Chem. Zentr.*, 1920, ii, 582—583).—It is found that sulphosalicylic acid gives a precipitate with urines rich in calcium which may easily be mistaken for a positive albumin reaction. The distinction between precipitated calcium sulphate and albumin is most readily made if the urine is previously diluted with at least half its volume of water; under these conditions calcium sulphate is not precipitated, whilst the albumin reaction is but little affected.

H. W.

Estimation of the Fibrin, Globulin, and Albumin Nitrogen of Blood Plasma. GLENN E. CULLEN and DONALD D. VAN SLYKE (*J. Biol. Chem.*, 1920, **41**, 587—597).—Fibrin is estimated by precipitation with calcium chloride under definite conditions from plasma containing 0.5% potassium oxalate. After thorough washing, the precipitate is submitted to the Kjeldahl process.

Albumin is estimated in plasma by precipitating the globulin by half saturation with ammonium sulphate, quantitatively removing the excess of ammonia in the filtrate, and making a Kjeldahl estimation on the residue. Non-protein nitrogen is estimated after removal of the plasma proteins by trichloroacetic acid. The plasma proteins are, therefore, separately estimated as follows: Fibrin N, directly; globulin N = total N - (filtrate N + fibrin N); albumin N = filtrate N - non-protein N.

J. C. D.

Crystallisation of Hæmatoporphyrin. TH. LOCHTE and E. DANZIGER (*Vierteljahrsschrift ger. öffentl. Sanitätswesen*, **59**, 140—143; from *Chem. Zentr.*, 1920, ii, 396—397).—The method described depends on Willstätter's process, and is effected in the following manner. The spot of blood is removed as completely as possible and covered in a small test-tube with about 0.5 c.c. of hydrobromic-glacial acetic acid solution; the tube is corked and heated at 40—50° for about fifteen minutes. After remaining for thirty-six to forty-eight hours at the ordinary temperature, water



sodium hydroxide solution sufficient to solution is faintly acidified with acetic to three times with ether. The ether is slowly on a small watch-glass, the residue is of the glass with two or three drops of with three to five drops of concentrated acid. The watch-glass is covered with a larger dish, and the solution is allowed to evaporate slowly; crystals generally form within one or two days.

H. W.

Colorimetric Estimation of Stercobilin. R. GOIFFON (*Compt. rend. Soc. Biol.*, 1920, **33**, 60; from *J. Pharm. Chim.*, 1920, [vii], **21**, 286—288).—Stercobilin, a reduction product of bilirubin, yields a red-coloured mercury compound which is soluble in dilute ammonia. To estimate stercobilin in faeces, 40 c.c. of a 10% faecal solution are heated for one hour at 50° with 5 c.c. of saturated mercuric chloride solution; the warm mixture is then treated with 2 c.c. of ammonia, diluted to 50 c.c., filtered, and the coloration of the filtrate compared with that of a standard. The latter may consist of a mixture of 100 c.c. of 10% cobalt chloride solution and 5 c.c. of potassium dichromate solution. The value 10 is suggested as a normal when the colorations of the test and standard solutions are of equal intensity. W. P. S.

Colloid-chemical Considerations regarding the Reductase Test for Milk. EGON EICHWALD (*Zeitsch. Nahr. Genussm.*, 1919, **38**, 359—361).—It is pointed out that the colloids in milk may play a part in the methylene-blue test for reductase in milk, and preliminary experiments show that the finer the state of division of the colloids (proteins and fat), the slower is the rate at which the blue colour is destroyed. W. P. S.

Reduced Eosin and Potassium Persulphate. LEON GOLDENBERG (*Anal. Soc. Quim. Argentina*, 1917, **5**, 264—266).—A colourless solution of reduced eosin may be obtained almost instantly and in the cold by weighing 1 gram of eosin, dissolving 2 grams of sodium hydroxide in 100 c.c. of water redistilled in glass, adding part of the eosin and 5 grams of chemically pure zinc dust, and shaking until decolorisation is complete. The remainder of the eosin is then added in portions whilst shaking. The stock solution thus obtained may be kept for two to three weeks, after which the eosin acquires a yellow colour on regeneration. For investigating oxydases, 0.5 c.c. of the above solution is made up to 100 c.c. The incomplete decolorisation of eosin by commercial zinc dust and distilled water condensed in metallic receivers is due to the presence of copper, traces of which are sufficient to induce catalytic re-oxidation of the reduced eosin.

The oxidising action of oxydases may be measured by comparison with a *N*/100-solution of potassium persulphate, 1 c.c. of which furnishes 0.00016 gram of oxygen. The quantity of oxydase which

causes reduced eosin to absorb 0.00016 gram at 37° is called the "oxydasogenous unit" which oxydases are determined as general comparison with the standard regenerated by reduced eosin obtained in the determination of hydrochloric acid, collected on a double filter, and redissolved on the filter in 2-3 c.c. of clear filtrate may now be matched against the persulphate

Quantitative Measurement of Lipase and Amylase in Pancreatic Juice. H. MAUBAN (*Compt. rend. Soc. Biol.*, 1920, 83, 130; from *J. Pharm. Chim.*, 1920, [vii], 21, 355-357).—0.2 c.c. of 0.2% starch solution are placed in each of ten tubes, and the first is added 1 drop of pancreatic juice, to the second 2 drops, and so on. The tubes and their contents are heated for five minutes, 0.25 c.c. of Fehling's solution is then added to each, and the mixtures are boiled for one minute, a small quantity of potassium ferrocyanide being added to prevent precipitation of copper. In this way is found the quantity of pancreatic juice necessary to produce sugar just sufficient to decolorise the measured quantity of Fehling's solution. Six or seven drops of normal pancreatic juice are usually required. W. P. S.

Estimation of Soil Acidity and Alkalinity by means of Indicators in the Field. EDGAR T. WHERRY (*J. Washington Acad. Sci.*, 1920, 10, 217-223).—The method of estimating the acidity or alkalinity of a soil in terms of P_H (A., 1919, i, 428) has been adapted for use in field tests, and a table has been constructed showing the reactions of the soil corresponding with the color changes of a series of indicators, each of which overlaps the next in the scale. Passing from extreme acidity to extreme alkalinity these indicators and their corresponding P_H values are: *Bromocresol-blue*, dull green, 3.5; brownish-green, 4.0; violet, 4.5; *methyl-red*, violet, 4.5; red, 5.0; orange, 5.5; yellow, 6.0; *bromocresol-purple*, yellow, 5.5; brownish-green, 6.0; violet, 6.5; purple, 7.0; *bromothymol-blue*, yellow, 6.0; greenish-yellow, 6.5; green, 7.0; blue, 7.5; *phenol-red*, yellow, 6.5; orange-yellow, 7.0; orange, 7.5; red, 8.0; violet-red, 8.5; *phenolphthalein*, colourless, 8.0; pale pink, 8.5; deep pink, 9.0; violet-red, 9.5. A definite quantity of the soil is shaken with neutral salt-free water, and the clear extract tested with successive indicators until one indicator shows an intermediate colour or the extreme colorations of two successive indicators overlap, and the corresponding P_H value is obtained from the table. By treating standard solutions of known ionic concentration and comparing the colorations with those given by soil extracts with the same indicators, specific acidities differing by a factor of $\sqrt[5]{10}$ or 1.59 ($P_H=0.2$) may be distinguished, but in practice values differing by a factor of $\sqrt{10}$ or 3.16 ($P_H=0.5$) are sufficiently accurate since the reactions of the soil from different parts of the root of the same plant may differ by a factor of 10 or more. C. A. M.

